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PHYSICAL REVIEW

AN EXPERIMENTAL STUDY OF THE RELATIVE INTENSITIES OF X-RAY LINES IN THE L-SPECTRUM OF URANIUM

By Samuel K. Allison

Abstract

The relative intensities of 17 lines in the L spectrum of uranium have been measured as a continuation of the work previously reported on thorium (Allison, Phys. Rev. **30**, 245 (1927)). Changes in the apparatus are described which reduce the magnitude of the corrections to be applied. The variation of the intensity of U $L\alpha_1$ with voltage has been studied and may be closely represented by $I=C(V-V_0)^{1.8}$, and with less accuracy by a function $I=C((V-V_0)/V_0-\log(V/V_0))$ developed by Rosseland. The observed results at 52.8 kv have been extrapolated to the relative intensities at voltages very much greater than the critical voltages. Important results are: (1) The lines $\gamma_3\gamma_2$ and $\beta_3\beta_4$, known in other elements to deviate from the sum rule predictions have equal intensities in uranium although a ratio 2:1 is predicted. (2) The lines $\gamma_6\beta_5$ are 17 times more intense in uranium than in tungsten due presumably to the filling of the 5_3 orbits in the intervening elements. (3) The lines $\gamma_4\gamma_5$ which are present in the tungsten spectrum are absent in the uranium and thorium spectra. It is shown that if Rosseland's function (above) holds for electron collisions in which the velocity of the impinging electron is great compared to the velocities of the electrons in the atom, that the relative intensities of lines of a multiplet under these conditions are equal to the product of the transition probability by the statistical weight of the initial state with only a slight correction. The results are:

	l	α_2	α_1	η	β_6	β_2	β_4	β_7	β_5	β_1	β_3	γ_8	γ_1	γ_3	γ_2	γ_4	γ_5
Rel. Int. at 52.8 kv	2.4	11	100	0.83	1.6	28	3.2	0.4	6.4	40.5	3.3	0	9.7	1.1	1.1	1.8	0
Rel. Int. at high V.	2.4	11	100	1.0	1.6	28	4.1	0.4	6.4	49.4	4.2	0	12	1.5	1.4	2.2	0

Introduction

THE relative intensities of x-ray lines in the L series of uranium have been measured as a continuation of the work on thorium previously reported.[1] Since the atomic numbers of thorium and uranium are close together it was expected that the results on uranium would serve to confirm those previously reported on thorium, and, in certain cases, to extend them, because certain lines can be resolved in the uranium L spectrum which cannot be separated in the thorium spectrum.

Apparatus

A general description of the apparatus has appeared in the previous paper on thorium. In the present work, certain changes were made in an attempt to reduce the correction factors as much as possible.

[1] Allison, Phys. Rev. **30**, 245 (1927).

(1) *Voltage.* The experiments on thorium were performed at 31.8 kilovolts. In order to reduce the correction necessary to change the observed intensities to the intensities at voltages high above the critical voltages of the L series, the present work was done at 52.8 kilovolts. In order to attain this voltage it was necessary that both the anode and cathode of the x-ray tube be charged above gound potential. This made it essential that the water cooling system be insulated, which was realised by siphoning the water back and forth between two 80 liter bottles.

(2) *Condenser.* The capacity of the condenser used in smoothing out the fluctuations in the 550 cycle high voltage circuit was increased. The condenser was divided into two parts of equal capacity which were connected in the anode and cathode sides of the circuit respectively. The capacity of each of these condensers was 0.045 micro-farad, and since the current through the x-ray tube was 5.5 milliamperes the calculated fluctüation was 244 volts or 0.5 percent at 50 kilovolts.

(3) *X-ray tube.* The x-ray tube was unchanged from the design illustrated in the preceding paper. The uranium was obtained through the kindness of Dr. W. D. Coolidge of the Research Laboratories of the General Electric Company. Several unsuccessful attempts were made to solder or weld the uranium to the face of the copper target. Finally through the courtesy of the Engineering Department of the University a piece of uranium was pressed into a copper block with a hydraulic press. This apparently made good thermal contact and served admirably as a target.

(4) *Ionization chamber.* The ionization chamber used in the experiments on thorium was 32 cm long and with a pressure of methyl iodide of 24 cm an appreciable fraction (25 percent) of the radiation of the harder lines in the L series passed through the chamber without being absorbed. In order to reduce this, a chamber 64 cm long was constructed and used. The fractional loss in the uranium $L\gamma$ lines was thus about 7 percent.

Results

Column 3 of Table I gives the observed, uncorrected, results on lines in the uranium L spectrum at 52.8 kilovolts. The measurements were made by comparing the heights of the tips of the peaks representing the lines above the level of the general radiation in the vicinity. In some instances the measurements were made in the second order. Here β_4 was easily separated from β_2 and also β_1 and β_5 were well resolved. An attempt to separate γ_6 and γ_3 more completely in the second order failed because of the weakness of the lines. The results given in column 3 are averages in each case of 3 or more trials.

Corrections to be Applied to Observed Results

The corrections to be applied to the observed results may be grouped under two headings (1) corrections due to absorption; (2) corrections due to the fact that the voltage used is comparable with the differences between the critical voltages of the L series.

The corrections due to absorption have been discussed in the previous paper, and no innovations in the method of making these corrections have been introduced. The magnitude of the corrections is less however, due, in the case of correction for absorption outside the ionization chamber, to the fact that the wave-lengths of the uranium L series are shorter than those of thorium, and, in the case of absorption inside the chamber, to the fact that a longer ionization chamber was used. The magnitude of these corrections is given in columns 4 and 5 of Table I. The pressure of the methyl iodide was 26 cm and the calculations were carried out as in the previous paper.

The question of correction for absorption in the target has been taken up in some detail by Jönsson[2] for soft x-ray lines. He has attacked the problem by measuring the intensity of certain soft x-ray lines, notably Al $K\alpha$ and Ag $L\alpha$ as a function of voltage. The theoretical derivation of these voltage-intensity curves involves three factors (1) the ionization function, or the number of ions produced per centimeter of path by an electron with a velocity of V kilovolts, (2) the law of decrease of velocity of an electron in traversing the target substance, and (3) the exponential law of absorption of the radiation produced in the target material itself. Jönsson has tested against his experimental observations the results of calculations involving two different ionization functions but otherwise the same. These ionization functions are those proposed by Bergen Davis[3] and by Thomson[4] and Rosseland.[5] The formula of Bergen Davis may be written

$$\eta = C(V - V_0)/V \tag{1}$$

where η is the number of ions (strictly the number of pairs of ions) formed per centimeter of path, V is the velocity of the impinging electron in kilovolts, V_0 is the energy in kilovolts required to remove the electron which is struck from the atom, and C is a constant whose dimensions are L^{-1}.

The formula of Rosseland may be written, neglecting relativity corrections, as

$$\eta = C\pi e^2 nN(1/V_0 - 1/V)/V \tag{2}$$

where N is the number of atoms per unit volume, n is the number of electrons in the group whose ionization potential is V_0 kilovolts, and e is the charge on the electron in electrostatic units. C is here a numerical constant entering because V and V_0 are defined in kilovolts instead of electrostatic units. This formula results from the calculations of Maxwell on classical theory, and depends on certain assumptions, an important one being that the velocity of the impinging electron is great compared to the velocities of the electrons in the atoms. This is certainly true in the passage of high-speed β-particles from radioactive sources through air, but it is not obvious that

[2] Jönsson, Zeits. f. Physik **43**, 845 (1927).
[3] Bergen Davis, Phys. Rev. **11**, 433 (1918).
[4] J. J. Thomson, Phil. Mag. **23**, 449 (1912).
[5] Rosseland, Phil. Mag. **45**, 65 (1923).

it is true in the target of an x-ray tube operated at moderate voltages where on the classical quantum theory the electrons in the groups under consideration are moving with velocities comparable to that of the incident particles. Nevertheless, Jönsson has found that function (2) in combination with the Thomson-Whiddington law and the exponential law of absorption of x-rays leads to a prediction of the intensity of soft x-ray lines as a function of voltage which agrees well with experiment, and is distinctly preferable to formula (1).

The correction to be applied for absorption in the target depends on the value of b in the Thomson-Whiddington law

$$V_x^2 = V^2 - bx \tag{3}$$

where V_x is the velocity in kilovolts at the depth x below the surface, and V is the incident velocity in kilovolts. The value of b has been investigated by Terrill.[6] The correction also depends on μ, the absorption coefficient of the target substance for the radiation produced. In the region of the L series, both b and μ[7] should have discontinuous jumps. Due to the great uncertainty of these values for uranium no correction has been made for absorption in the target.

The experimental results in column 6 of Table I are the relative intensities at 52.8 kilovolts. In order to be able to predict the relative intensites at other voltages the law of variation of intensity with voltage must

TABLE I. *Results*

Line	ν/R Uranium	Obs. Int. 52.8 kv	Corr. for abs. outside ion. chamber	Corr. for % absorbed in chamber	Corr. Int. 528 kv	$\left\{\frac{V-V_0^{\alpha}}{V-V_0}\right\}^{1.8}$	Rel. Int. high V voltage Uranium	Thorium (previous paper)
l	856	2.1	1.13	1.00	2.4	1.00	2.4	3.6
α_2	990	11	1.02	1.00	11	1.00	11	12
α_1	1003	100	1.00	1.00	100	1.00	100	100
η	1135	.88	.94	1.00	.83	1.22	1.0	1.8
β_6	1159	1.7	.93	1.00	1.6	1.00	1.6	1.4
β_2	1211	30	.91	1.01	28	1.00	28	26
β_4	1222	3.5	.91	1.01	3.2	1.28	4.1	
β_7	1238	.4	.91	1.01	.4	1.00	.4	.4
β_5	1258	6.8	.90	1.02	6.4	1.00	6.4	
β_1	1269	44	.90	1.02	40.5	1.22	49.4	62*
β_3	1286	3.6	.90	1.02	3.3	1.28	4.2	3.3
γ_5	(1436)	0			0		0	0
γ_1	1487	10.4	.87	1.09	9.7	1.22	12	14
γ_2	1508	1.2	.86	1.10	1.1	1.28	1.5	1.5
γ_3	1526	1.1	.86	1.11	1.1	1.28	1.4	
γ_6	1538	1.9	.86	1.11	1.8	1.22	2.2	
γ_4	(1588)	0			0		0	0

* This value includes β_5

be known. As the exciting voltage is increased, the relative intensities of two lines belonging to different excitation groups approaches a limiting value,

[6] Terrill, Phys. Rev. **22**, 101 (1923).

[7] Kellström, Zeits. f. Physik **44**, 269 (1927).

which may be calculated from the results at a single voltage if the law of variation with voltage is known.

The circles in the graph in Fig. 1 give the experimentally observed values of the intensity of U $L\alpha_1$ at various values of $V-V_0$. The accuracy of these points is not all that can be desired, especially in the higher voltages. No electrostatic voltmeter was available which would read over the entire

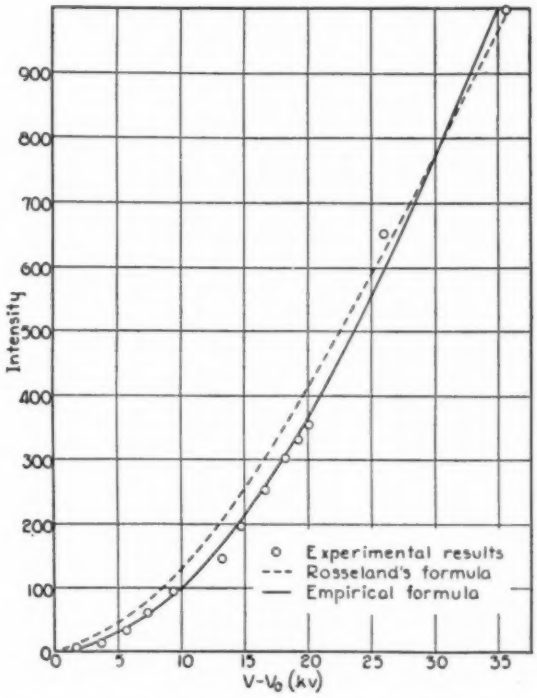

Fig. 1. Variation of intensity of U $L\alpha_1$ with voltage. $V_0=17.11$ kv.

range, and the voltages had to be found in each case by measuring the short wave-length limit of the spectrum, which though very accurate, is very tedious.

Previous investigators, such as Webster and Clark,[8] and Jönsson,[9] have empirically expressed the law of variation as

$$I=C(V-V_0)^m \tag{4}$$

Webster and Clark found $m=1.5$ for platinum and rhodium; Jönsson found $m=1.7$ for tungsten, and in the preceding paper on thorium $m=2$ was found from three points on the curve. The solid curve in Fig. 1 is a plot of (4) for $m=1.8$ where C is chosen so that the solid curve fits the points at $V-V_0=20$. The dashed curve in Fig. 1 is a plot of the integrated ionization function (2). This integration is performed as follows. The total number

[8] Webster and Clark, Phys. Rev. **9**, 571 (1917).
[9] Jönsson, Zeits. f. Physik **36**, 426 (1926).

of ions formed by an electron entering the target with a velocity of V kilovolts before it has been slowed down below a velocity of V_0 kilovolts will be given by

$$\int_V^{V_0} \eta dx = C\pi e^2 nN \int_V^{V_0} (1/V_0 - 1/V) dx/V$$

The voltage may be introduced as the only variable from (3) with the result

$$N_i = C\pi e^2 nN\left(\frac{V-V_0}{V_0} - \log \frac{V}{V_0}\right) \tag{5}$$

where N_i is the total number of atoms thrown into the ith state of ionization. Since the intensity of a line whose initial state is the state i should be proportional to N_i, the equation should give the variation of the intensity with voltage. The curve was plotted in the form

$$N_i = C\left(\frac{V-V_0}{V_0} - \log \frac{V}{V_0}\right)$$

by choosing C so that the ordinate for $V - V_0 = 34$ fell near a straight line connecting the last two experimental points. This was done because in the theoretical background of Eq. (5) the assumption is made that the velocity of the electrons in the atom is negligible in comparison with that of the impinging electron.

It is seen that the plot of Rosseland's function agrees fairly well with the slope of the last two measured points but gives values too high for the points at lower voltage. The empirical function fits the points in general better than the Rosseland function.

If R is the observed ratio of the intensity of a line whose critical voltage is V_0 to the intensity of $L\alpha$ whose critical voltage is V_0^α, then R_∞, or the ratio at high voltage may be easily shown to be, in terms of Eq. (4)

$$R_\infty = R\left(\frac{V-V_0^\alpha}{V-V_0}\right)^{1.8} \tag{6}$$

and in terms of Eq. (5)

$$R_\infty = R\frac{V-V_0^\alpha(1+\log (V/V_0^\alpha))}{V-V_0(1+\log (V/V_0))} \tag{7}$$

The corrections to be applied to lines having L_{21} and L_{11} as initial states are 1.22 and 1.28 respectively from Eq. (6), and 1.31 and 1.39 respectively from Eq. (7). In Table I the corrections are given from the empirical functions (4) and (6) since it is desired to keep the experimental results as free from theory as possible. If the corrections were made on the basis of Rosseland's equation the intensities of lines ending in L_{21} and L_{11} would be raised about 7 percent.

In the last two columns of Table I are given the resultant intensities at high voltage obtained from obserations on uranium and thorium.

Discussion of Results

Interest in the relative intensities of the L series lines may at present be grouped under three heads. (1) The variation of the relative intensities of corresponding lines in the spectrum as a function of the atomic number of the radiator. (2) The relative intensities of lines constituting a series, that is, of lines in a given element as a function of the change in azimuthal and total quantum numbers. (3) The relative intensities of members of multiplets.

Information on the variation with atomic number and with the change of azimuthal and total quantum number may be obtained from Table II. The variation of the intensities of $\beta_3\,\beta_4$, $\beta_5\gamma_6$ and γ_4 and γ_5 with atomic number are especially interesting. Table II, together with previous results of Jönsson[10] on lighter elements shows that the intensities of these lines decrease

Table II. *Variation of relative intensities of multiplets as a function of atomic number and as a function of the change in total and azimuthal quantum numbers.*

Lines	Δn_k	Theory (Wentzel)	Obs. 74W Jönsson	Obs. 90Th	Obs. 92 U		
$\beta_1\alpha_1\alpha_2$	$3_3\rightarrow 2_2$	(1.00)	(1.00)	(1.00)	(1.00)		
ηl	$3_1\rightarrow 2_2$	.02	.03	.03	.02	Total	Hα
$\beta_3\beta_4$	$3_2\rightarrow 2_1$	.21	.08	.03	.05†	3−2 (1.00)	Bongers (1.00)
$\gamma_1\beta_2$	$4_3\rightarrow 2_2$	.43	.18	.23	.25		
$\gamma_8\beta_6$	$4_1\rightarrow 2_2$	.01	.01	.01	.01	Total	
$\gamma_2\gamma_1$	$4_2\rightarrow 2_1$	.12	.02	.02	.02	4−2 .26	Hβ .13
$\gamma_6\beta_5$	$5_3\rightarrow 2_2$		.003		.05		
$\gamma_8\beta_7$	$5_2\rightarrow 2_2$			.003	.003	Total	Hγ
γ_4	$5_2\rightarrow 2_1$		.004	0	0	5−2 .05*	.02

† This value is more accurate than the value .03 given for thorium because β_4 had to be guessed at in thorium.

* This value applies to the uranium spectrum.

with respect to other lines in the L series with increasing atomic number. This behavior is not true of the lines $\gamma_3\gamma_2$ which have the same initial state (L_{11}). No adequate explanation has as yet been advanced for this behavior.

The behavior of the lines $\beta_5\gamma_6$ can be explained to a certain extent by Bohr's theory of the periodic system. It is seen that the relative intensity of these lines is 17 times greater in uranium than in the tungsten L spectrum. The electron transitions which give rise to these lines come from the levels $O_{32}O_{33}$. In tungsten these levels are in the process of filling, while in uranium they are filled. The behavior of these lines is thus in accord with the observations of Allison and Armstrong[11] and Jönsson[12] on similar cases.

[10] Jönsson, Zeits. f. Physik **46**, 383 (1928).

The case of the lines γ_4 and γ_5 is interesting and apparently anomalous. These lines exist as moderately weak lines in the tungsten L spectrum but all attempts to find them in the thorium and uranium L spectra have failed. A curve taken in search of these lines is shown in Fig. 2. These lines have been reported in the spectrum of uranium at 42 kilovolts by Dauvillier[13] but their presence could not be confirmed. No values of wave-lengths for these lines are given in Siegbahn's book "The Spectroscopy of X-Rays."

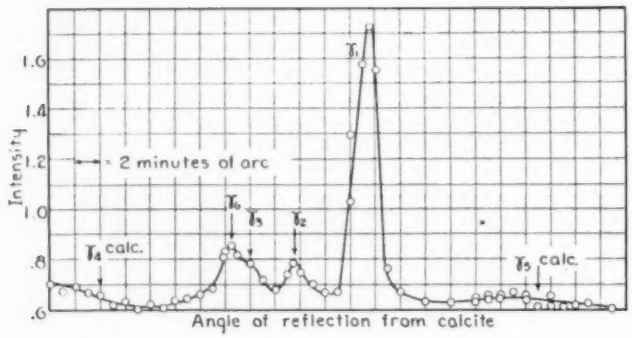

Fig. 2. Uranium L spectrum, γ group.

In Table II the variation in intensity as a function of the change in total and azimuthal quantum numbers is given in a manner that shows the relation between the x-ray spectra and the alkali arc and hydrogen atom spectra. Thus in the L series lines involving transitions from M to L shells we have the components of the non-degenerate $H\alpha$ line. The theoretical values are those given by Wentzel[14] on the basis of the Schrödinger mechanics. For comparison the observations of Bongers[15] on the corresponding lines in the Balmer series are included.

The fact that the relative intensities of members of multiplets which involve transitions whose initial state is L_{11} are exceptions to the Burger-Dorgelo rules has been known for some time by the work of Allison and Armstrong[11] and Jönsson.[16] Further information on these interesting mul-

[11] Allison and Armstrong, Phys. Rev. **26,** 714 (1925) see p. 722.

[12] Jönsson, Zeits. f. Physik **41,** 221 (1927). It is interesting to note that the results of Jönsson in this paper indicate that the $N_{32}N_{33}$ levels are completely filled for the first time at the element Ag 47. Spectroscopic evidence (McClennan and Smith, Proc. Roy. Soc. **A112,** 110 (1926)), on the other hand, has shown that the $N_{32}N_{33}$ orbits are filled at Pd 46 whose lowest term is $^1S_0$. This discrepancy may very likely be accounted for by the fact that in the solid state the $N_{32}N_{33}$ orbits in Pd are greatly distorted by the van der Waals forces, while in Ag 47 most of the distortion is in the orbit O_{11}.

[13] Dauvillier, Jour. d. Physique **3,** 221 (1922).

[14] Wentzel, Naturwissenschaften **14,** 621 (1926). In a private communication, Wentzel has pointed out that the theoretical values in question were calculated on the basis of equal excitation of all the L levels, and that correction for this may explain the large discrepancy in the experimental and theoretical values of transitions ending in L_{11}.

[15] Reported by Ornstein, Physik. Zeits. **28,** 688 (1927).

[16] Jönsson, see ref. 9 and Zeits. f. Physik **41,** 801 (1927).

tiplets could not be obtained from the thorium spectrum because of interference of other lines. In the case of uranium it was possible to obtain β_3 and β_4, ($M_{21,\ 22} \rightarrow L_{11}$) free from other lines, and the ratio of β_3 to β_4 is 100:98 instead of 100:50. These lines have been investigated in Mo, Rh, Pd, Ag, Sn, W, by Jönsson[16] and found to have a ratio 100:63.3. The results of this investigation show an increase in intensity of the weaker member with increasing atomic number. A curve showing $L\gamma_3$ and γ_2 is shown in Fig. 2. The intensity of γ_3 is uncertain because of the presence of γ_6 but appears to be about equal to that of γ_2. Table III shows the relative intensities of some multiplets in thorium and uranium.

It has been stated that the intensities of multiplets involving the initial states L_{21}, L_{22} obey the sum rules, but the measurements here show exceptions to these rules, namely $\gamma_5\beta_6$ and $\gamma_6\beta_5$. From the results in Table III, it may be stated that while in these elements the relative intensities of

TABLE III. *Comparison of observed intensities and sum rule predictions.*

Lines	Transitions	Theory	Obs. Th	Obs. U
$\gamma_3:\gamma_2$	$N_{21}N_{22} \rightarrow L_{11}$	100:50		100:107
$\beta_3:\beta_4$	$M_{21}M_{22} \rightarrow L_{11}$	100:50		100:98
$\gamma_6:\beta_6$	$N_{11} \rightarrow L_{21}, L_{22}$	50:100	0:1.4	0:1.6
$\eta:l$	$M_{11} \rightarrow L_{21}, L_{22}$	50:100	50:100	46:100
$\gamma_6:\beta_5$	$O_{32}O_{33} \rightarrow L_{21}, L_{22}$	50:100		34:100
$\gamma_1:\beta_2$	$N_{22}N_{33} \rightarrow L_{21}L_{22}$	50:100	53:100	43:100
$\beta_1:\alpha_1:\alpha_2$	$M_{32}M_{33} \rightarrow L_{21}L_{22}$	56:100:11	62*:100:12	49:100:11

* This value includes β_5.

$\beta_1\alpha_1\alpha_2$, $\gamma_1\beta_2$ and ηl are given to a fair degree of approximation by the sum rules, the deviations of $\gamma_3\gamma_2$, $\beta_3\beta_4$, and the two doublets mentioned above are definitely greater than the experimental errors. It may be remarked that the anomalous cases are those in which one or both of the orbits involved are highly elliptic. Jönsson has noted that the lines $\beta_3\beta_4$ are broader than the more intense lines and has mentioned a possible connection between this and the ellipticity of the orbits involved.

Recently Ornstein, Eymers, and Coelingh[17] and Ornstein and Burger[18] have shown that the sum rule is only an approximate rule holding for small frequency differences, and that in certain cases the observed values of intensities of widely separated multiplets divided by the fourth power of the frequency obey the sum rules. It is obvious that this cannot be the explanation of the deviations in Table III.

CALCULATION OF TRANSITION PROBABILITIES AND STATISTICAL WEIGHTS FROM INTENSITY DATA ON THE L-SERIES

The results given here for thorium and uranium are stated in terms of the relative intensities at voltages much greater than the critical voltages of the L series. It can be shown that if the classical mechanics is adequate to

[17] Ornstein, Eymers and Coelingh, Zeits. f. Physik **44**, 653 (1927).

[18] Ornstein and Burger, Zeits. f. Physik **40**, 403 (1926).

describe the impacts of fast electrons against electrons relatively at rest (J. J. Thomson's ionization function Eq. 2) that these relative intensities are related to the transition probabilities and statistical weights in the following way:

$$E_1S_1/E_2S_2 = I_1V_{01}\nu_2/I_2V_{02}\nu_1 \tag{8}$$

where E represents transition probability, S the statistical weight of the initial state, I the observed intensity at high voltage, V_0 the critical voltage of the line, and ν the frequency of the line.

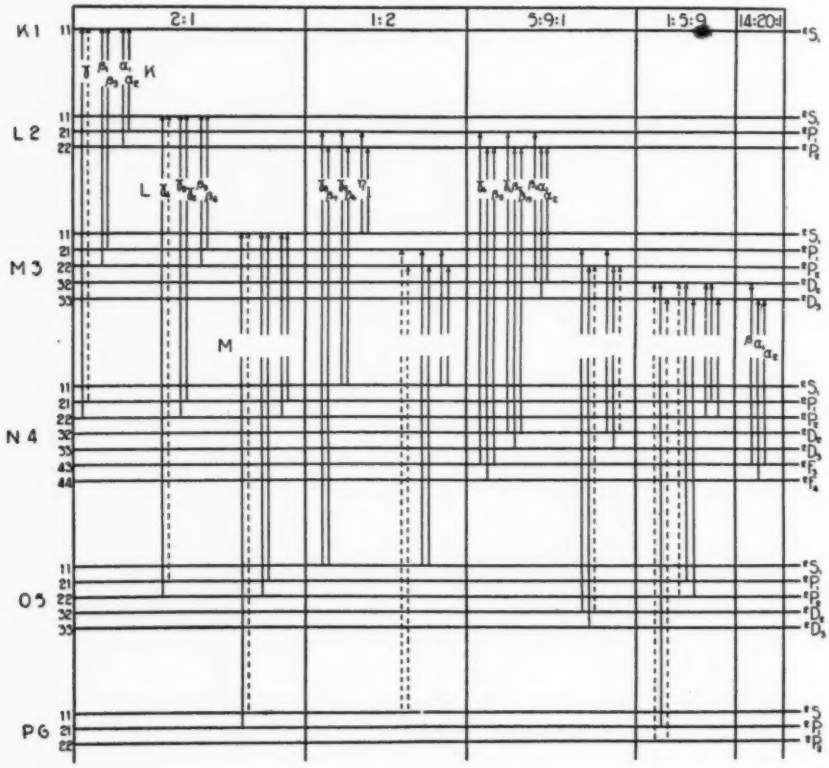

Fig. 3. X-ray energy level diagram showing lines in the K, L, M series and their grouping into multiplets. The sum rule intensities of the multiplets are given in the divisions at the top of the diagram. At the right the analogous optical levels in the alkali arc spectrum are given.

On the quantum theory the intensity of a line is given by

$$I = EN_ih\nu \tag{9}$$

where N_i is the number of atoms in the initial state ready to radiate the line in question. Eq. (5) gives us information concerning relative values of N_i at high voltages, namely (taking the limit as V approaches infinity of the ratio of the N_i's for two different levels as given by Eq. (5)),

$$N_{i1}/N_{i2}=n_1V_{02}/n_2V_{01} \tag{10}$$

n_1 and n_2 from Eqs. (2) and (5) are the numbers of electrons per atom in the groups in question. The classical theory does not predict equal excitation of two levels of the same electron content by high speed beta-particles, but excitation in the inverse ratio of the ionization potentials. If we think of the groups L_{21} and L_{22} respectively, the numbers n_1 and n_2 are 2 and 4. It is known that on the Hund theory of spectral terms it is unnecessary to consider sub-divisions of electrons having the same azimuthal and total quantum numbers. The analogous quantities to the numbers 2 and 4 are the statistical weights $(2j+1)$ of the terms, and so we set $n_1/n_2=S_1/S_2$. Making this substitution, Eqs. (10) and (9) give (8).

The correction to be applied to the relative intensities of members of the $L_{21}L_{22}$ multiplets in order to obtain relative values of ES is very small since the terms V_{01}/V_{02} and ν_2/ν_1 of Eq. (8) almost completly neutralize each other. We may therefore say that within the limits of experimental error the values of Table I represent the product of transition probability and statistical weight of the initial state for each member of a multiplet.

In a recent paper Jönsson[10] has used an equation based on Eqs. (2) and (5) to correct the observed values of the intensities in the L series of Ag, Pd, Rh, Mo. His procedure corresponds to dividing the observed intensities by the corresponding value of the variable part of the right-hand member of Eq. (5). The corrected results given by him are then the relative intensities for equal excitation of all levels but the equation of Rosseland which he uses predicts that such equal excitation will never occur. In order to change the values given by him in Table 3 of his paper to the relative intensities at high voltage, they must be multiplied by the factor V_{01}/V_{02} of Eq. (8) where V_{01} is the critical voltage of the level L_{22}. For instance the values of α_1/β_1 and β_2/γ_1 for Ag are reported as 100/59 and 100/57 respectively. If the suggested correction is made, they become 100 /55 and 100/53 respectively, which brings them nearer to the sum rule values.

UNIVERSITY OF CALIFORNIA,
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INTERPRETATION OF ATOMIC STRUCTURE FACTOR CURVES IN CRYSTAL REFLECTION OF X-RAYS

By G. E. M. Jauncey and W. D. Claus

Abstract

In a previous paper (Phys. Rev., May, 1928) the authors showed that, for certain values of D the grating space of a crystal of rocksalt, the area under a radial electron distribution (or U) curve for chlorine rose above 19 electrons. This result was obtained both from Havighurst's experimental F curve and from F values calculated for a model chlorine ion, these calculated values being modified to take into account the Compton effect. This result seemed perplexing, inasmuch as both the real ion and the model ion have but 18 electrons. The present paper is a further discussion of this point. It is proved that for any symmetrical atom F values, calculated according to the classical theory and unmodified for the Compton effect but multiplied by the Debye temperature factor, give U curves the areas under which never exceed the number of electrons assumed in the model. It is also shown that an unsymmetrical atom gives F values which behave in the same way. But, since both experimental and modified theoretical F values (that is, modified to take account of the Compton effect) give U curves the areas under which do exceed the true number of electrons for certain values of D, there is an indication that the Compton effect is involved in the experimental values. The truth of this indication would invalidate the use of the Fourier analysis method as now applied. The present paper also develops the Fourier integral as a quick method of calculating a U curve from a model atom on the classical theory. It is shown that a U curve calculated from Compton's formula

$$U=(8\pi r/D)\sum_{1}^{\infty}(nF_n/D)\sin(2\pi rn/D)$$

for a Fourier series is a very close approximation to the true U curve given by the Fourier integral

$$U(r)=8\pi r\int_0^{\infty} xF(\lambda x/2)\sin 2\pi rx\,dx$$

where F is the same function of $(\lambda x/2)$ as F in the series formula is a function of $\sin\theta$. An analysis by the Fourier integral of a model supposed to have all the electrons concentrated at the center together with the Debye temperature factor shows that $U(r)$ represents the distribution of electrons about a lattice point and not about the center of the atom.

I. Introduction

In A recent issue of the Physical Review,[1] the authors have discussed the criticisms of Havighurst[2] on the method of Williams[3] and Jauncey[4] for correcting for the Compton effect in calculations of the theoretical atomic structure factor (or F) values to be expected for a given atom model. In our previous paper, we have raised objection to the practice by some authors of using values of the grating space of a crystal which were inordinately large

[1] Jauncey and Claus, Phys. Rev. **31**, 717 (1928).
[2] R. J. Havighurst, Phys. Rev. **31**, 16 (1928).
[3] E. J. Williams, Phil. Mag. **2**, 657 (1926).
[4] G. E. M. Jauncey, Phys. Rev. **29**, 757 (1927).

and entirely fictitious as there is no possibility of obtaining an experimental F value for the first order with one of these large grating spaces. However, assuming that the use of these large values of the grating space is allowable, we were led to construct Table IV of our previous paper. In this table are shown values of the area under a radial electron distribution (or U) curve for chlorine from $r=0$ to $r=D/2$, for various values of D, where D is the grating space. Table IV shows for both the experimental F curves (reasonable extrapolations being used for the F values at both the small and large angles) and the theoretical F values calculated for our model and modified for the Compton effect that the number of electrons under a U curve is over 19 even though there are only 18 electrons in our theoretical model and though we also extrapolated to $F=18$ at $\sin\theta=0.00$ in the experimental F curve. Referring to Table IV, we see that there are more electrons under the experimental curve for $D=4.44$A than for $D=7.10$A. It is difficult to conceive how there could be less electrons between $r=0$ and $r=D/2$ for $D=7.10$A than for $D=4.44$A. Since writing our previous paper, it has occurred to us that this peculiar variation of the area under a U curve may give some insight into the need for a Compton effect correction. Before examining into whether this peculiar variation of the area proves the need for a Compton effect correction, we shall consider the case for the variation of the area with D for classical scattering of x-rays from a model atom possessing spherical symmetry. We shall show that F values calculated classically and without a Compton effect correction for a model atom give areas under U curves which approach the number of electrons assumed in the model as D approaches infinity but that for other values of D the area is always less (although it may only be slightly less) than the number of electrons assumed in the atom. Further, we shall examine the effect of different extrapolations for the chlorine experimental F values, all extrapolations, however, ending at $F=18$ for $\sin\theta=0.00$, and we shall show that it is impossible to choose a reasonable extrapolation for which U curves for various values of D always have an area equal to or less than 18 electrons. At present we believe that the experimental F values for chlorine, for instance, are not sufficiently accurate to prove definitely that a value of D can always be found to give more than 18 electrons, but the F values found by Havighurst certainly do show this effect.

A second point which we wish to discuss is the closeness of the agreement between a curve as found for a model atom, assuming the classical theory, when a series of discrete F values are inserted in Compton's[5] formula

$$U=(8\pi r/D)\sum_{1}^{\infty}n(F_n/D)\sin(2\pi nr/D) \qquad (1)$$

and a U curve found by means of a Fourier integral when D in Eq. (1) is made to approach infinity. The U curve found by means of the Fourier integral is the correct U curve while that obtained from the Fourier series in Eq. (1) is an approximation.

[5] A. H. Compton, X-Rays and Electrons, p. 164.

A third point to which we wish to call attention is that Paragraph 43 of Compton's "X-Rays and Electrons" is headed "Radial Distribution in Atoms." The subject matter of this paragraph leads one to infer that a U curve obtained from Eq. (1) gives the radial distribution of the electrons relative to the center of an atom in the crystal. However, we believe that the radial distribution is relative to a lattice point of the crystal and not to the center of an atom of the crystal.

II. Classical Scattering from a Model Atom

Case I. As the simplest kind of atom, let us take a model consisting of Z electrons concentrated at the center. The f values (Havighurst's notation) for such a model are constant and equal to Z, while the F values are given by $Z\exp(-b\sin^2\theta)$. In our previous paper, as in Havighurst's paper, $b=2.39$ for $\lambda=0.71$A reflected from rocksalt. Now $\sin\theta=n\lambda/2D$ so that $F_n=Z\exp(-n^2b\lambda^2/4D^2)$. For brevity we shall represent the Debye factor by $\exp(-n^2a^2)$ where $a^2=b\lambda^2/4D^2$. The area under a U curve from $r=0$ to $r=D/2$ according to Compton[5] is

$$A=-2\sum_{1}^{\infty}(-1)^n F_n \tag{2}$$

Putting the values of F_n for our model in Eq. (2), we have

$$A=-2Z\sum_{n=1}^{n=\infty}(-1)^n\exp(-n^2a^2) \tag{3}$$

We shall now determine how A varies with a and, therefore, with D. The series

$$S_1=\exp(-a^2)-\exp(-2^2a^2)+\exp(-3^2a^2)-\cdots \tag{4}$$

may be written

$$S_1=\sum_{n=1}^{n=\infty}[\exp\{-a^2(2n-1)^2\}-\exp\{-a^2(2n)^2\}] \tag{4a}$$

By Cauchy's theorem $S_1<I_1$ for $a>0$ where

$$I_1=\int_0^{\infty}[\exp\{-a^2(2x-1)^2\}-\exp\{-a^2(2x^2)\}]dx \tag{5}$$

By putting $y=(2x-1)$ in the first term of the integrand and $z=2x$ in the second term, we have

$$I_1=(1/2)\int_{-1}^{\infty}\exp(-a^2y^2)dy-(1/2)\int_0^{\infty}\exp(-a^2z^2)dz \tag{6}$$

and since we are dealing with definite integrals

$$I_1=(1/2)\int_0^{1}\exp(-a^2x^2)dx \tag{7}$$

By the mean value theorem

$$I_1=(1/2)\exp(-a^2\xi^2) \tag{8}$$

where $0<\xi<1$. For $a>0$, $\exp(-a^2\xi^2)<1$ and $I_1<\frac{1}{2}$ and hence also $S_1<\frac{1}{2}$.* From this it follows that A in Eq. (3) can never be greater than Z no matter what value of D is taken.

Case II. We shall now consider a model made up of Z electrons all on a sphere of radius s, the temperature factor being supposed to be constant and equal to unity. Compton[6] gives the atomic structure factor in this case as $F=Z\sin(4\pi s\sin\theta/\lambda)/(4\pi s\sin\theta/\lambda)$, or since $\sin\theta=n\lambda/2D$, $F_n=Z(\sin n\phi)/n\phi$ where $\phi=2\pi s/D$. The area A then becomes

$$A=(2Z/\phi)\{\sin\phi-(1/2)\sin 2\phi+(1/3)\sin 3\phi-(1/4)\sin 4\phi+\cdots\} \tag{9}$$

The series

$$S_2=(1/\phi)\{\sin\phi-(1/2)\sin 2\phi+(1/3)\sin 3\phi-(1/4)\sin 4\phi+\cdots\} \tag{10}$$

has the property that $S_2=1/2$ for $-\pi<\phi<\pi$. This can be seen at once by expressing the function $y=\phi/2$ as a Fourier series in sines of multiples of ϕ between $\phi=-\pi$ and $\phi=\pi$. For all reasonable values of s in our model $s<D/2$ and hence $\phi<\pi$, so that $A=Z$ in Eq. (9) for all values of D. In an actual numerical calculation the series S_2 converges slowly and so a large number of terms has to be taken, and to permit this, the wave-length of the x-rays has to be small so that the limiting value of n as given by the Bragg equation may be large. Hence, we again find that A can never be greater than Z no matter what value of D is taken so long as λ is small.

Case III. As a third model, we shall consider the case of Z electrons on a sphere of radius s, the center of the sphere thermally vibrating so that there is a Debye temperature factor $\exp(-b\sin^2\theta)$. We now have $F_n=Z\exp(-n^2a^2)\cdot(\sin n\phi)/n\phi$ and hence

$$A=-(2Z/\phi)\sum_{n=1}^{n=\infty}(-1)^n(1/n)\sin n\phi\exp(-n^2a^2) \tag{11}$$

and we are led to the consideration of the series

$$S_3=\sum_{n=1}^{n=\infty}\left[\frac{\exp\{-a^2(2n-1)^2\}\sin(2n-1)\phi}{(2n-1)\phi}-\frac{\exp\{-a^2(2n)^2\}\sin 2n\phi}{2n\phi}\right] \tag{11a}$$

Again by Cauchy's theorem $S_3<I_3$ for $a>0$ where

$$I_3=\int_0^\infty\left[\frac{\exp\{-a^2(2x-1)^2\}\sin(2x-1)\phi}{(2x-1)\phi}-\frac{\exp\{-a^2(2x)^2\}\sin 2x\phi}{2x\phi}\right]dx$$

$$=(1/2)\int_0^1\frac{\exp(-a^2x^2)\sin x\phi\,dx}{x\phi} \tag{12}$$

* We are indebted to Professor W. H. Roever of the Mathematics Department of Washington University for this proof.

[6] A. H. Compton, Phys. Rev. 9, 29 (1917).

By the mean value theorem

$$I_3=(1/2)\exp(-a^2\xi^2)\cdot(\sin\xi\phi)/\xi\phi \qquad (12a)$$

where $0<\xi<1$. Hence as in Case I, $I_3<1/2$ and also $S_3<1/2$. Again A cannot be greater than Z no matter what value of D is taken.

Case IV. In the ion of chlorine we have K, L, and M electrons. If each of these groups is moving in circular orbits which are oriented at random, the F values for each group when inserted in Eq. (2) will give values of A which are not greater than the number of electrons assumed in each respective group. If the F values for all the groups are added together, then A will not be greater than the total number of electrons in all the groups assumed in the model. Further, even if some of the electrons are revolving in ellipses or in more complicated orbits, then so long as the axes of these orbits are oriented in random directions, such orbits can be considered as supplying dN electrons between the spheres of radii r and $r+dr$ and the F values for these dN electrons when inserted in Eq. (2) will not give more than dN electrons. Hence, we see that any atom model which on the average possesses spherical symmetry must give values of A which can never be greater than the number of electrons assumed in the model, whatever value of D we may choose.

Referring again to Table IV of our previous paper, we see that the experimental F curve for chlorine leads to an area of 19.74 electrons at $D=4.44$A, while at $D=35.5$A, the area is 18.08 electrons. The question arises as to whether this difference of 1.66 electrons is due to errors in reading the F values off the experimental F curve. We drew our experimental F curve on graph paper in such a way that 20 millimeter divisions along the ordinates measured an F value of unity, while 20 millimeter divisions along the abscissae measured $\sin\theta=0.1$. We could thus read our F values to 0.05 and we estimated to one-fifth of a millmeter so that we estimated our F values to 0.01. To test our accuracy we calculated the theoretical F values for the model of our previous paper, these F values, however, being uncorrected for the Compton effect. These F values were calculated for the same angles as the angles for the experimental F values shown in Table I of the previous paper and were calculated to the second decimal place. The curve was then drawn so as to pass through an F value of 18 at $\sin\theta=0$. Such an F curve from $\sin\theta=0.617$ where $F=0.52$ was then extrapolated to zero at $\sin\theta=1.00$. The largest value of A in Eq. (2) was found to be 18.20 for $D=3.94$A. The correct value of A is slightly less than 18 so our error of reading from the F curve is such as to produce an error of 0.20 electrons in the area under a U curve. But the greatest value of A in Table IV of the previous paper is 19.74 for the experimental F curve and this is too great to be explained as due to errors in reading F values from the curve. We next tried different extrapolations both at small angles and at large angles for the experimental F curve. The F value for first order reflection for $D=4.44$A, or $\sin\theta_1=0.08$, is an extrapolated value on the experimental F curve. A reasonable extrapolation, such as is shown by the dashed line in Fig. 1, gives an area greater

than 19 electrons for this value of D. To make $A=18$ electrons for $D=4.44$A, it is necessary to make $F_1=14.70$. As the F value for sin $\theta=0.109$ is 13.40, this makes an awkard kink in the F curve at sin $\theta=0.109$ as shown by the broken and full curves in Fig. 1. Nor does this improve matters at other values of D. Also, for the extrapolation at the large angles, an F value which will bring A nearer 18 for one value of D will make A still greater than 18 for another value of D. We have thus been unable to find an extrapolation either at the small or the large angles which will give values of A never greater than 18, the F value assumed at sin $\theta=0.00$. If the F value at sin $\theta=0.00$ is assumed to be 17, which is the value for a neutral chlorine

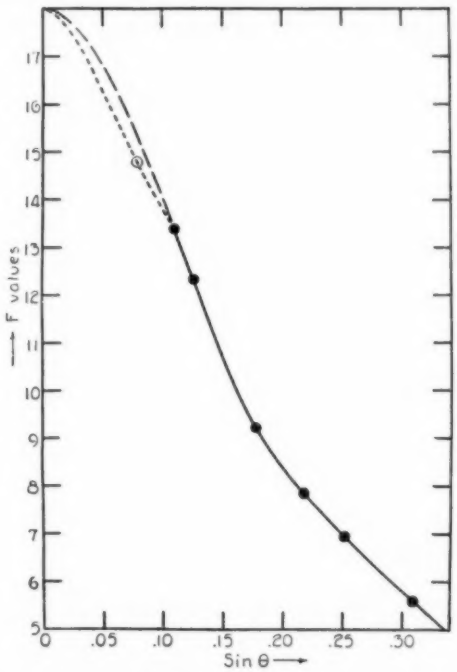

Fig. 1. Experimental F curve for chlorine, showing extrapolations. Broken and dashed curves, extrapolations; black circles, experimental F values; white circle, extrapolated point to give 18 electrons for $D=4.44$A.

atom, the situation is still worse; but, if F is assumed to be 20 at sin $\theta=0.00$, then it might be possible to find an extrapolation which would give F values such that A was always less than 20 electrons. This is an unreasonable number of electrons according to our present ideas. We are convinced that Havighurst's experimental F curve shows the peculiarity that a value of D can be found such that the area under the U curve is greater than the number of electrons assumed or believed to be present in the ion or atom.

III. Modification of Classical Scattering by the Compton Effect

Since in Section II of this paper we have shown that classical scattering from a model assumed to possess spherical symmetry on the average requires

that the area under a U curve be always less than the number of electrons assumed in the model, and since on the other hand the experimental F values do not show this result, we believe that this proves that either the atoms do not on the average possess spherical symmetry or that the Compton effect has to be taken into account.

We shall first consider the effect on the area under a U curve when an unsymmetrical model is taken. As an example of an unsymmetrical atom, we may take an atom which consists of a nucleus and Z electrons, the nucleus being in a crystal plane and the Z electrons remaining at a certain distance z from the plane. If one half of the atoms are orientated with their electrons above the plane and one half below the plane, the atomic structure factor[7] is given by $F_n = Z\cos(4\pi z \sin\theta/\lambda) = Z\cos n\phi$ where $\phi = 2\pi z/D$.

Eq. (1) is only valid for an atom possessing spherical symmetry but if the F values given by $F_n = Z\cos n\phi$ are treated as coming from a symmetrical atom, then the area under the U curve so obtained is given by Eq. (2) and we are led to the series

$$S_4 = \cos\phi - \cos 2\phi + \cos 3\phi - \cos 4\phi + \cdots \tag{13}$$

This series is obtained by differentiating $S_2\phi$ and since $S_2 = 1/2$, we have $S_4 = 1/2$ for $-\pi < \phi < \pi$. When the temperature factor is included, we have $F_n = Z\exp(-n^2a^2)\cos n\phi$ and we are led to the series

$$S_5 = \sum_{n=1}^{n=\infty} \left[\exp\left\{-a^2(2n-1)^2\right\}\cos(2n-1)\phi - \exp\left\{-a^2(2n)^2\right\}\cos 2n\phi\right] \tag{14}$$

Proceeding as in Case III we have
$S_5 < I_5$ for $a > 0$ where

$$I_5 = (1/2)\int_0^1 \exp(-a^2x^2)\cos x\phi\, dx \tag{15}$$

By the mean value theorem

$$I_5 = (1/2)\exp(-a^2\xi^2)\cos\xi\phi \tag{15a}$$

where $0 < \xi < 1$. Hence $I_5 < 1/2$ and also $S_5 < 1/2$ and $A \not> Z$. Any unsymmetrical atom can be considered as made up of dN electrons at a distance between z and $z+dz$ from a crystal plane, dN being a function $Zp(z)dz$. These dN electrons give values which when substituted in Eq. (2) make $A \not> dN$. Summing for all distances from the crystal plane, we find that even for an unsymmetrical atom the F values calculated on the basis of the classical theory possess the property that the right hand side of Eq. (2) is never greater than the number of electrons assumed in the atom.

We shall now consider the effect of the correction due to the Compton effect on the value of the right hand side of Eq. (2). It may be a coincidence but it is nevertheless a fact that when A is calculated by means of Eq. (2) for different values of D for Havighurst's experimental and the modified

[7] A. H. Compton, X-Rays and Electrons, p. 121.

theoretical (corrected for the Compton effect) F curves, the value of A in both cases becomes greater than Z for certain values of D. To take a particular case, we shall consider the L electrons in the model of the chlorine ion as given in our previous paper. The atomic structure factor for these electrons is given by $F=Z\ y\ H'$ where

$$y=0.5-0.635 \sin\theta+0.0965/\sin\theta$$

and

$$H'=1-y\{1-\sin(4\pi s \sin\theta/\lambda)/(4\pi s \sin\theta/\lambda)\} \tag{16}$$

and where $s=0.29$A the radius of the L orbit. Replacing $\sin\theta$ by $n\lambda/2D$, this leads to the series

$$S_7 \equiv \sum_1^\infty y_n H_n' \tag{17}$$

The value of S_7 has been plotted against $\sin\theta_1$ where θ_1 is the angle at which first order reflection occurs for a grating space D and the curve is shown in Fig. 2. Unlike all the previous series, it is seen that S_7 may be greater than $1/2$ and so the F values for a model atom corrected for the Compton effect

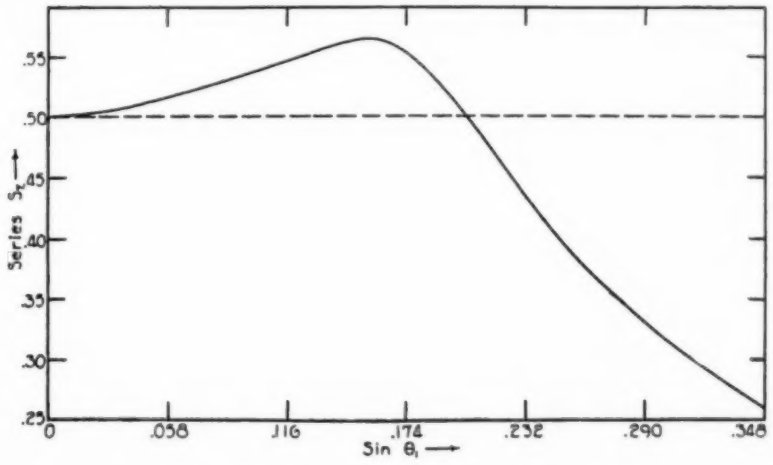

Fig. 2. Curve showing that series S_7 may exceed $1/2$.

lead to values of the right hand side of Eq. (2) which for particular values of D are greater than Z, the number of electrons assumed in the atom. If it can be definitely shown that the experimental F values possess the property that a value of D can be found such that A in Eq. (2) can be made greater than Z the number of electrons which we can reasonably expect to be present in the atom then it seems to us that something in addition to the classical theory is required. Since the Compton effect correction to a model gives F values such that A can be made greater than Z, we believe that this gives us an excellent method for testing whether the Compton effect does or does not enter into the regular reflection of x-rays by crystals. Havighurst's F

values seem to us therefore to show the need for a Compton effect correction. If the Compton effect has to be taken into account, the present method of Fourier analysis is invalid as we showed in our previous paper and Eq. (1) has no particular meaning.

IV. Fourier Integral

If D in Eq. (1) approaches infinity, the series of Eq. (1) approaches the Fourier integral

$$U(r)=8\pi r\int_0^\infty xF(\lambda x/2)\sin 2\pi rx\,dx \tag{18}$$

where F in the Fourier integral is the same function of $(\lambda x/2)$ as F in the series is a function of $\sin\theta$. The Fourier integral form has an advantage over the series in that when a U curve for a model atom is desired it may happen that for the model the value of the right side of Eq. (18) expressed as a function of r can be found by integration and the labor of finding the value of the series in Eq. (1) is saved.

For instance, we shall apply the Fourier integral to Case I, Section II of this paper. This gives

$F(\sin\theta)=Z\exp(-b\sin^2\theta)$, so that $F(\lambda x/2)=Z\exp(-b\lambda^2x^2/4)=Z\exp(-a^2x^2)$ where $a^2=b\lambda^2/4$ and Eq. (18) becomes[8]

$$U(r)=(4\pi^2\pi^{1/2}Z/a^3)r^2\exp(-\pi^2r^2/a^2) \tag{19}$$

$U(r)$ is a maximum when $r=a/\pi$, that is, the most probable displacement of the atom due to the thermal vibrations is a/π and this may be represented by α so that

$$U(r)=(4Z/\alpha^3\pi^{1/2})r^2\exp(-r^2/\alpha^2) \tag{20}$$

The form of the right hand side of Eq. (20) shows that the distribtuion of the thermal displacements of the atom is a Maxwell distribution. This is as it should be because the form of the Debye temperature factor can be obtained from the assumption of thermal displacements distributed according to the Maxwell law.[9] Since $\alpha=a/\pi$ we have $\alpha=\lambda(b)^{1/2}/2\pi$. Since $b=2.39$ for $\lambda=0.71$A reflected from rocksalt at room temperature, the numerical value of α is 0.175A in good agreement with a value of 0.20A estimated by James and Firth[10] by another method. Since in this case the electrons of the model are concentrated at the center of the atom and since $U(r)$ is a maximum when $r=\alpha=0.175$A, we see that $U(r)$ cannot mean the distribution of electrons relative to the center of the atom but must be relative to a lattice point of the crystal. $U(r)$ represents the distribution of the excursions of the atom from this lattice point.

[8] Peirce's Integral Tables, No. 508.

[9] See Compton, X-Rays and Electrons, p. 170.

[10] James and Firth, Proc. Roy. Soc. **A117**, 62 (1928).

Applying the Fourier integral to the Case III, Section II of this paper, we obtain

$$U(r)=(Z/\alpha s\pi^{1/2})r\{\exp\left[-(r-s)^2/\alpha^2\right]-\exp\left[-(r+s)^2/\alpha^2\right]\} \qquad (21)$$

We are now in a position to find the U curve for the model atom of our previous paper, when the F values are uncorrected for the Compton effect. This curve is shown in Fig. 3. The points shown are the values of U found from Eq. (1) when $D=3.06$A or $\sin\theta_1=0.116$. It will be seen that the points fall almost exactly on the curve and this shows the accuracy of the Fourier series method because a curve plotted from Eq. (1) is almost indistinguishable from a curve plotted from the Fourier integral Eq. (18). It will be noticed that only two humps occur. The hump due to the K electrons is obliterated. This again brings out the point that a U curve gives the

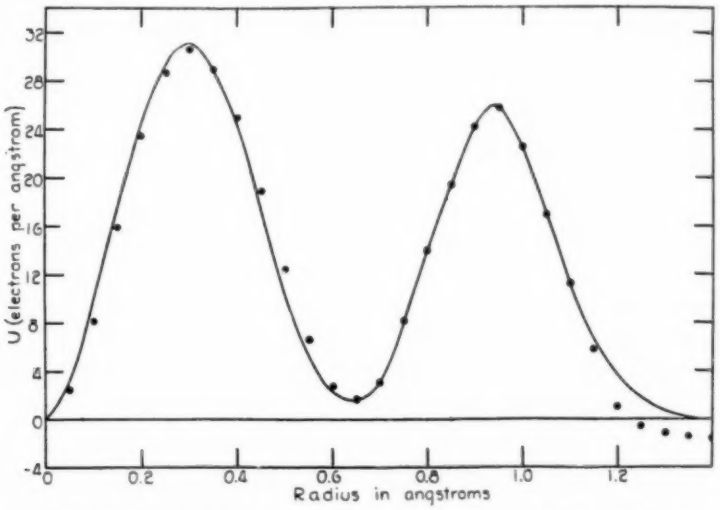

Fig. 3. Electron distribution as given by the Fourier integral and the Fourier series. Full curve, Fourier integral; black circles, Fourier series.

distribution relative to a lattice point. The most probable thermal displacement is 0.175A while the radius of the K orbit is 0.033 in our model. The K and L electrons are merged together giving a maximum at 0.300A which is somewhat greater than the radius of 0.29 assumed for the L orbit, while the M electrons give a maximum at 0.940A instead of at 0.925A the value of the radius assumed for the M orbit. It is thus seen that the thermal vibrations cause the maxima for the L and M electrons to come somewhat further out than assumed in the model, but, of course, this is to be expected since a U curve gives the distribution relative to a lattice point and not relative to the center of the atom.

WASHINGTON UNIVERSITY,
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April 6, 1928.

THE SCATTERING OF X-RAYS FROM GASES

By Charles S. Barrett

Abstract

Intensity of the scattering of molybdenum x-rays from carbon dioxide, argon, oxygen, nitrogen, helium, and hydrogen at scattering angles from 20° to 155°.— All except hydrogen show excess scattering (with helium it may, however, be due to nitrogen present as an impurity): the excess scattering extends to larger angles from the primary beam as the atomic number of the gas increases and as the wavelength increases. This excess scattering appears to be mostly, if not wholly, due to interference arising within the atom. Destructive interference is prominent with argon, and seems probable (though it is very weak) with oxygen, carbon dioxide, and nitrogen. Mark and Schocken's results, which indicated scattering by gases follows the $(1+\cos^2\theta)$ law, are not confirmed. Hydrogen follows within experimental error the quantum theory prediction of Breit, Dirac, Gordon, and Waller. Even when the K_α rays of molybdenum are used the scattering from hydrogen does not show the irregularities predicted by Debye's interference theory.

Introduction

THE intensity of x-rays scattered in different directions by an atom has been calculated on the basis of electromagnetic theory for a number of different atomic models by Darwin,[1] Debye,[2] Schott,[3] Compton,[4] Glocker and Kaupp,[5] and Glocker.[6] Interference in the x-rays scattered from the groups of electrons postulated in these models should cause a deviation from the distribution of intensity calculated for an electron scattering independently $(1+\cos^2\theta)$. In addition to this interference arising within the atom, there may exist interference due to a regular spacing of the atoms in a molecule, and also that due to a preferred spacing of molecules among themselves. The phenomenon of excess scattering may be the result of all these causes when solids and liquids are used as the scattering material. Debye[7] has calculated that the latter cause may be eliminated by using a perfect gas as the scatterer. Therefore excess scattering from a monatomic perfect gas can be ascribed only to the structure of the atom. Jauncey[8] has obtained excess scattering in the case of the diffuse scattering from a crystal. To reduce this scattering to the scattering from a single molecule requires the use of Debye's temperature factor. Jauncey concludes from his experiments that this theoretical factor of Debye's is greatly in error. It is hardly possible

[1] C. G. Darwin, Phil. Mag. **27**, 315 (1914).
[2] P. Debye, Ann. d. Physik **46**, 809 (1915).
[3] G. A. Schott, Proc. Roy. Soc. **A96**, 395 (1920).
[4] A. H. Compton, Wash. Univ. Studies **8**, 99 (1921).
[5] R. Glocker and M. Kaupp, Ann. d. Physik **64**, 541 (1921).
[6] R. Glocker, Zeits. f. Physik **5**, 54 (1921).
[7] P. Debye, Mathematical Journal of Physics **4**, 133 (1925); also Phys. Zeits. **28**, 135 (1927).
[8] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922).

at present to determine definitely how a single atom scatters by experiments of the type Jauncey performed, while it is possible to do so by scattering from gases.

This paper is a report of an experimental determination of the distribution of x-rays scattered from hydrogen, helium, nitrogen, oxygen, argon, and carbon dioxide. In spite of numerous suggestions by Debye, Schott, and Compton that experiments of this type should give important information on the nature of atoms and radiation, the only previous attempt seems to be that of Mark and Schocken.[9] They scattered Mo $K\alpha$ rays (crystal reflected) from carbon dioxide and argon, and found very nearly a $(1+\cos^2\theta)$ distribution of intensity, or scattering function as it has been called, for both gases. No evidence was found for excess scattering from an individual atom of argon and practically none from an individual molecule of carbon dioxide. They report the scattering of carbon dioxide as slightly greater than argon from 30° to 50°, and slightly less than argon from 140° to 160°.

Because of the presence of the Compton effect, there is an increasing amount of modified radiation as the atomic weight of the scatterer decreases. Woo[10] predicts, on the basis of his experiments, the scattering from hydrogen and helium to be almost completely modified. The scattering function for these elements should therefore be that predicted by the quantum theories (unless possibly the modified ray is not truly incoherent). The older forms of quantum theory do not give a unique prediction for this function. Perhaps the most satisfactory of these is Compton's.[11] Breit,[12] on the basis of the correspondence principle; Dirac,[13] with the matrix mechanics of Heisenberg and Born; Gordon[14] and Waller[15] from the standpoint of the deBroglie-Shroedinger wave mechanics, all agree in predicting this function to be

$$I_\theta = \frac{Ine^4(1+\cos^2\theta)}{2m^2r^2c^4(1+\alpha \operatorname{vers}\theta)^3}, \qquad \alpha = \frac{h\nu}{mc^2}. \tag{1}$$

where I_θ is the intensity of the scattered rays at the angle θ from the primary beam, and at the distance r from the scatterer, which is composed of n electrons of charge e and mass m. The primary beam, of intensity I, is assumed unpolarized.

A test of the old vs. the new quantum theories was recently performed by Dr. Bearden and the author,[16] based on the fact that the latter predicts the angle at which x-rays become polarized by scattering to be 90°, while the

[9] H. Mark and K. Schocken, Naturwiss. **15,** 139 (1927).

[10] Y. H. Woo, Phys. Rev. **27,** 119 (1926).

[11] A. H. Compton, Phys. Rev. **21,** 491 (1923). (A summary of these theories is given in Compton's "X-Rays and Electrons," D. Van Nostrand Co., New York City (1926), pp. 296–305.)

[12] G. Breit, Phys. Rev. **27,** 362 (1926).

[13] P. A. M. Dirac, Proc. Roy. Soc. **A111,** 405 (1926).

[14] W. Gordon, Zeits. f. Physik **39,** 117 (1926).

[15] Ivar Waller, Phil. Mag. **4,** 1228 (1927).

[16] C. S. Barrett and J. A. Bearden, Phys. Rev. **29,** 352 (1927).

older theories give a polarizing angle dependent upon the wave-length and less than 90°. Our experiment gave 90° independent of the wave-length, within experimental error, and confirmed the theory on which Eq. (1) is based. Thus it appears that hydrogen and helium should scatter according to Eq. (1) except at small angles where some unmodified scattering may occur. With heavier gases there may be angles at which the electrons of an atom scatter almost independently and yet not give rise to completely modified scattering. One would expect in this case a scattering function intermediate between Eq. (1) and the classical formula for independent scattering of unpolarized x-rays by electrons. The latter is

$$I_\theta = \frac{Ine^4(1+\cos^2\theta)}{2m^2r^2c^4} \tag{2}$$

Apparatus

The apparatus used is drawn to scale in Fig. 1. A water-cooled molybdenum-target x-ray tube was operated at currents up to 60 milliamperes and voltages up to 63 kv while connected to mercury pumps. The radiation from this was passed through various types of filters at F, through slit S_1, and entered a metal chamber C through a window of thin celluloid. The gas to be studied was admitted to C at pressures ranging from less than one millimeter to several atmospheres. Secondary radiation from a small volume of this gas passed through slits S_2 and S_3 into an ionization chamber. The ionization current produced in this chamber was taken as a measure of the intensity of the scattered radiation at the different angles θ from the direct beam.

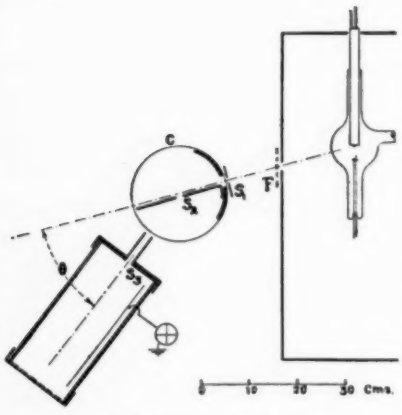

Fig. 1. Diagram of apparatus.

The x-ray tube was operated from kenotron-rectified a.c., and a balanced circuit was used to minimize fluctuations in current and voltage.[17] By having a voltmeter and milliameter constantly in sight and controls convenient, the error due to power-line fluctuations was kept low. Most of the readings were taken between 2:00 and 5:00 A.M., when power-line fluctuations were at a minimum.

The gas chamber C, 20 cms in diameter, 11 cms deep, was lined with lead foil and had a vertical lead partition extending across it parallel to the primary beam. The partition contained a rectangular slit S_2 (1.2 cms wide by 2.4 cms high) opposite the center of the chamber. A window 2.4 cms high was cut most of the way around the chamber and covered with clear cellu-

[17] J. A. Bearden, Phys. Rev. **29**, 20 (1927).

loid 0.55 mm thick, through which the x-rays could enter and leave the chamber with negligible absorption. When evacuated and disconnected from the oil pump, the leak in this chamber was of the order of a centimeter of pressure per hour. Slit S_1 was rectangular, 8 mms wide and 2.1 cms high and was placed so that about 5 mms intervened between the edge of the primary beam of x-rays and the partition carrying S_2. The slit S_1 was 11 cms from the center of the chamber. Slit S_3 at the ionization chamber was rectangular, 1.3 cms wide by 2.3 cms high, and was 18 cms from S_2. A lead tube of the same cross section extended from this slit toward S_2 to shield the ionization chamber from spurious radiation.

The ionization chamber was cylindrical, 12 cms in diameter and 30 cms long and was filled with methyl bromide. A voltage of about 350 was applied to it, and the ionization currents were measured with a Compton electrometer by the rate of deflection method. Measurements in the range 20°–100° (i.e. those plotted in Fig. 7) were made with the tube and its lead box as shown; the focal spot was 38 cms from the center of the scattering chamber. Later measurements, extending from 20° to 155° (Figs. 2 to 6) were made with the focal spot moved to 40 cms. The partition for these measurements was placed on the opposite side of the primary beam from that shown in Fig. 1, and the ionization chamber also used on that side, but the dimensions of the apparatus remained practically unchanged.

Some experiments were done with the total unfiltered radiation from the tube. Operating at 63 kv and 24 ma, the value of the effective wave-length (determined by absorbtion in 0.65 mm aluminum) was 0.48A; operating at 45 kv (approx) and 35 ma, it was 0.50A. With a 1.3 mm aluminum filter at F, Fig. 1, the x-rays at 63 kv, 24 ma had an effective wave-length of 0.39A. These conditions are the ones used in obtaining Figs. 2 to 7. For experiments where a monochromatic beam was desired, balanced filters of zirconium oxide and strontium oxide were used according to a method suggested by Professor P. A. Ross.[18] Each filter was adjusted to such thickness that it absorbed the same amount of the K_β radiation. They were then found to be well matched at all wave-lengths except those between their K absorption limits. Placing first one then the other in the primary beam and taking the difference of the intensity transmitted, a highly monochromatic spectrum was obtained.[19] With the large cross section of the beam available by this method, the energy used was much greater than could be obtained with the usual crystal reflection method. The accuracy was impaired, however, by the fact that it was necessary to deal with differences of readings rather than with the readings themselves.

The gases used were from tanks: the hydrogen was said by the manufacturers to be electrolytic and to contain only 0.03 percent oxygen as an impurity; the oxygen, 0.1 percent impurity. The purity of the helium (obtained from the U. S. Government) was not known, but it undoubtedly contained several percent of nitrogen. The removal of this was attempted

[18] P. A. Ross, Phys. Rev. **28**, 425 (1926).

[19] C. S. Barrett, Proc. Nat. Acad. Sci. **14**, 20 (1928).

by passing it slowly through two traps in series containing cocoanut charcoal and immersed in liquid air. It was necessary to pass the helium through these traps slowly while the chamber was below atmospheric pressure, so the leakage of air into the chamber may have contaminated the purified helium. The argon was about 95 percent pure, and the nitrogen and carbon dioxide probably somewhat better than this. All gases were admitted to the scattering chamber through a dehydrating tube and plugs of glass wool. In the case of every gas except helium, then, the scattering from impurities should have been negligible. The ratio of the intensities of the scattering from different gases at the same pressure and angle support this conclusion. The gas pressures in the scattering chamber were measured with a mercury manometer and were kept constant to one percent during readings.

The volume of the gas effective in scattering at different angles was not the same. To correct for this, the path of the primary beam was filled with light solid substances such as cotton batting, small waxed paper cylinders, and bran. The scattering at each angle was then obtained. These substances were then made into narrow vertical cylinders and placed in the primary beam with the scattering chamber removed, and with the x-ray tube operating under the same conditions as before. The ratio of the scattering of a substance outside the chamber to its scattering at the same angle inside gave a correction factor which, multiplied by the original gas readings for that angle, reduced them to the value that would be obtained from a small cylinder of gas in the primary beam. Corrections for spurious scattering from the walls, ionization leak, etc., had to be made in all measurements, and amounted on the average to five or ten percent of the total current. The materials used in this calibration were of course only approximately uniform in density when placed in the chamber. Though precautions were taken against errors due to this fact, nevertheless the accuracy of the gas readings was considerably lowered by multiplication by this factor. The relative scattering of two gases at the same pressure and angle could be determined with a probable error of one to two percent when the intensities due to them were nearly the same. Because of the difficulty in obtaining the correction factors for 20° and 155° they are somewhat less reliable than those for the other angles. After reduction by this correction factor, the probable error was 3 to 5 percent, though of course the accuracy of the *ratio* of the two remained the same.

Procedure and Results

Fig. 2 shows the ionization current obtained when the ionization chamber was set at a particular angle and the pressure of oxygen in the scattering chamber was varied. It shows clearly that, over the whole range of angles, the scattering was proportional to the gas pressure. Thus taking the scattering of a gas in the chamber at a certain pressure and subtracting the scattering at zero pressure, one has left only the true scattering from the gas.

The curve R in Fig. 3 is the volume correction factor mentioned previously. The data in Fig. 2 are multiplied by the appropriate values from

this R curve and plotted as the solid curve of Fig. 3. The classical theory for the scattering from a single electron, Eq. (2), is plotted as the broken curve of Fig. 3 marked C, and the quantum theory, Eq. (1), is the broken curve Q. All oxygen values have been multiplied by an arbitrary factor (the same for all angles) to make the solid curve fall somewhere between C and Q

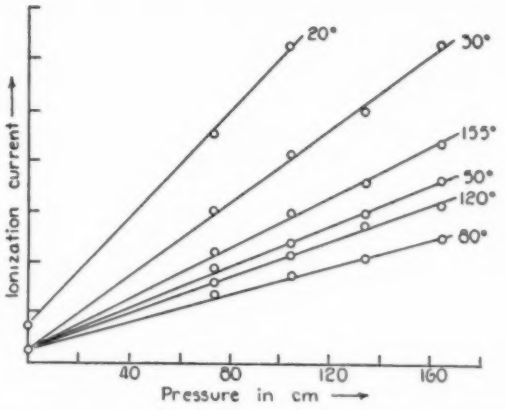

Fig. 2. Scattering from oxygen at different pressures.

at the larger angles. As there is both modified and unmodified radiation present at these angles in unknown proportions, one does not know exactly where in this range the solid curve should fall. In Fig. 3 excess scattering is evident below about 60°. The lowness of the 80° scattering possibly indicates that there is destructive interference in this neighborhood.

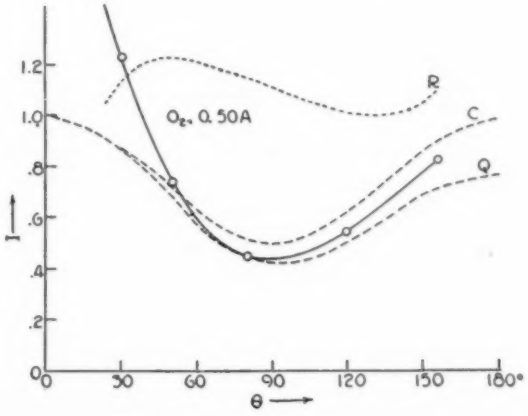

Fig. 3. Scattering from oxygen.

Figs. 4 and 5 represent data obtained in a similar manner for the gases oxygen, argon, nitrogen, and carbon dioxide at two different wave-lengths. The same pressure was used for each gas, and the intensity of the primary beam remained the same, for all the data in each figure. In these figures the scattering of each gas is divided by its number of electrons per molecule;

i.e., the curves represent the scattering per electron. The evidence is convincing for the presence of both constructive and destructive interference in x-rays scattered from argon. Remembering that the proportion of modified radiation present increases with the angle of scattering, one would expect the curve representing absence of interference to lie relatively nearer the curve Q, in the region between C and Q, at large angles than at small angles.

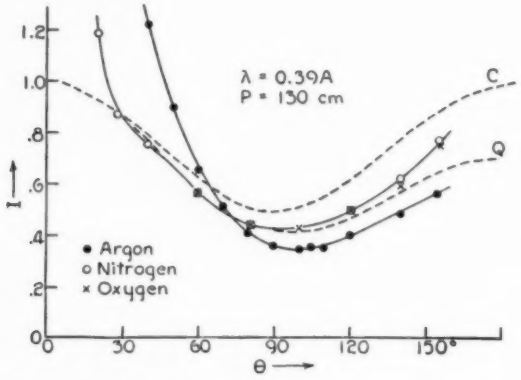

Fig. 4. Scattering from argon, nitrogen, and oxygen.

In the light of this, Figs. 3, 4, and 5 may indicate the presence of a little destructive interference for the gases oxygen, nitrogen, and carbon dioxide in the region around 60°–90°.

Further evidence that there is interference in x-rays scattered from argon is the variation with wave-length of the scattering from this gas illustrated

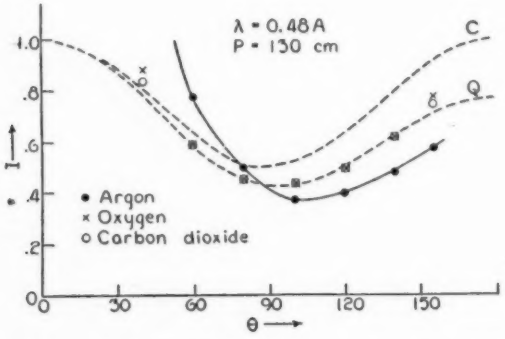

Fig. 5. Scattering from argon, oxygen, and carbon dioxide.

in Fig. 6. The curves for three different effective wave-lengths, $\lambda_1 > \lambda_2 > \lambda_3$, are arbitrarily reduced to the same value at 100°. In this figure the volume correction factor has not been used. Another test of the same type was made with two different wave-lengths, over the range 30°–150°. In all cases the excess scattering increased and extended to larger angles with increase in wave-length, as predicted by the classical theory.

Another series of experiments, giving the scattering per electron for hydrogen, helium, nitrogen, oxygen, and argon, is summarized in Fig. 7. Constructive and destructive interference from argon is again prominent. The fact that excess scattering becomes concentrated nearer the direct beam as the atomic number of the scatterer decreases may be interpreted as evidence of increasing size of the atom with decreasing atomic number. The helium curve shows excess scattering; but due to the possible presence of nitrogen as an impurity, one hesitates to ascribe this excess solely to the helium itself. Helium and hydrogen scatter equally from 60° to 100°. Hydrogen follows the broken line of Fig. 7, which represents Eq. (1) indicating completely modified radiation.

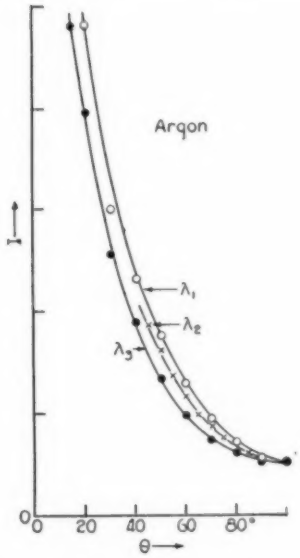

Fig. 6. Scattering from argon as a function of wave-length ($\lambda_1 > \lambda_2 > \lambda_3$).

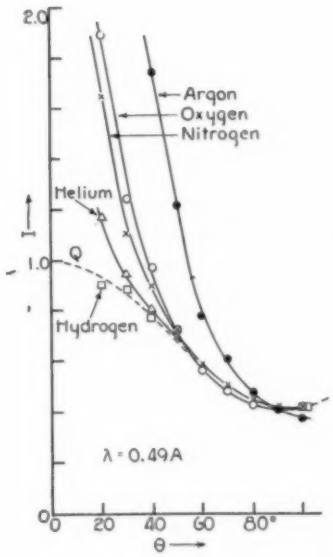

Fig. 7. Scattering of argon, oxygen, nitrogen, helium, and hydrogen.

Previous experiments[19] over the range 20°–90° with oxygen, carbon dioxide, and hydrogen showed oxygen (and also carbon dioxide, whose values could not be distinguished from those of oxygen) to have excess scattering below 60° which varied with the wave-length, while the scattering from hydrogen was practically independent of the wave-length. The accuracy of these experiments was not as great as that of the curves shown here, but in the case of hydrogen it was sufficient to show the absence of interference effects of the type predicted by Debye and others.

The author wishes to express his gratitude to Professor A. H. Compton for his continued encouragement and numerous suggestions, and to the Coffin Foundation, established by the General Electric Company, for the grant of a fellowship to carry out this investigation.

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April 10, 1928.

THE FIRST SPARK SPECTRUM OF PALLADIUM (Pd II)

By A. G. Shenstone

Abstract

An analysis of Pd II is given which differs completely from the previous one made by McLennan and Smith. The terms found include $4d^2D(4d^9)$; $5s^{4\&2}F$, $^{4\&2}P$, ^2D, $^2G(4d^85s)$; all the related triads from the structure $4d^85p$; $6s^{4\&2}F$, $^4P_3$, $^2G_4(4d^86s)$; and fragments of terms due to $4d^85d$. Zeeman effects of the majority of the lines have been measured and approximate g-values found for the low and middle sets of terms. The g-values depart largely from Landé's values, as do also the term intervals. Evidence is given that the term predicted by theory, $5s^2S(4d^85s)$, is present but it has not been fixed with respect to the other terms. The lowest term $4d^2D$ gives lines in the vacuum region and was found by Mr. H. E. White, of Cornell University, from plates taken there. The ionization potential is calculated from the s^4F terms as 19.8 volts from $4d^9$ to $4d^8$. As in other spectra of this type there is some indication in the limits of the component series that the Hund theory of limits is incorrect.

AN ANALYSIS of the first spark spectrum of palladium has been given by McLennan and Smith.[1] The great dissimilarity between that analysis and the one found for the spark spectrum of nickel[2] led the author to examine the previous analysis of Pd II in detail. The following paper presents a new analysis which differs in every detail from that given by McLennan and Smith.

The spectrum has been measured by a number of observers, but the old measurements of Exner and Haschek have been utilized in the present analysis, because they are in general very reliable and in addition are more complete. The author has also had the advantage of the measurements and intensity estimates made by Dr. Meggers of the Bureau of Standards, to whom he is very grateful. In the region below λ2250, new measures have been made using an Hilger E.1 quartz spectrograph, the standards being the copper spark lines calculated by the author.[3] In addition the whole spectrum has been photographed in order to make observations of the relative intensities in the spark and in long arc exposures. The lines may be divided into a number of very distinct classes: (1) lines which are sharp and of comparable intensity in the arc and spark exposures; (2) lines which are diffuse in the spark and appear with lower intensity in the arc; and (3) lines which are sharp in the spark and which appear faintly or not at all in the arc. Class 1 contains the lines due to transitions to the low set of terms; Class 2, lines due to transitions to the middle terms; and Class 3, lines due to higher ionizations. The appearance of some lines of Class 3 in the arc is probably due to the very unsteady nature of the arc which allows high potential differences to exist momentarily. The wave-lengths of the lines of Class 2 are of

[1] J. C. McLennan and H. G. Smith, Proc. Roy. Soc. **A112**, 110 (1926).
[2] A. G. Shenstone, Phys. Rev. **30**, 255 (1927).
[3] A. G. Shenstone, Phys. Rev. **29**, 380 (1927).

the order of 0.08 angstroms longer in the spark than in the arc. This is the usual experience with diffuse spark lines.

The term structure of Pd II can be simply predicted from the Hund theory. The low terms should be ^2D from the structure $4d^9$: ^4F, ^2F, ^4P, ^2P, ^2D, ^2G, ^2S from the structure $4d^8 5s$. The middle set of terms should be the triads associated with each of these terms, excluding $^2D(d^9)$ which, of course, has no triad of its own but may combine with all the other triads. In particular, the strongest lines should be due to the transitions from the triad $^{4\&2}D$, F, $G(d^8p)$ to $^{4\&2}F(d^8s)$. The leading lines of the three multiplets can be assigned immediately as λ2488.92, λ2296.53, λ2231.59, the only three spark lines found by Meggers and Laporte[4] as reversals in the under-water spark. The three corresponding diffuse lines λ2539.44, λ2776.85, λ2878.01, due to the combinations with the next series member $^4F_5(4d^8 6s)$, yield immediately the approximate I.P. = 16.7 volts, from $4d^8 5s$ to $4d^8$. The remaining terms were found by the usual method of frequency differences.

TABLE I. *Term Table for Pd II.*

No.	Term	Desig.	g Obs.	g Landé
1	−25081.	$4d^9D_3$		
2	−21542.	$4d^9D_1$		
3	0.0	$5s^4F_4$	1.33	1.33
4	2013.3	$5s^4F_4$	1.24	1.24
5	3846.0	$5s^4F_3$	1.03	1.03
6	4864.6	$5s^4F_2$	.40	.40
7	7196.9	$5s^2F_4$	1.20	1.14
8	9341.0	$5s^2F_3$	1.10	.86
9	11200.5	$5s^4P_3$	1.36	1.60
10	12284.0	$5s^4P_2$	1.47	1.73
11	13421.4	$5s^4P_1$	2.73	2.67
12	14490.1	$5s^2D_3$	1.20	.80
13	16117.3	$5s^2D_2$	1.30	1.20
14	18566.8	$5s^2P_2$	1.25	1.33
15	18858.8	$5s^2P_1$	.69	.67
16	19424.7	$5s^2G_4$	1.11	1.11
17	19532.9	$5s^2G_4$	.89	.89
18	40166.0	ap^4D_4	1.43	1.43
19	42218.0	ap^4G_5	1.17	1.17
20	42881.2	ap^4D_3	1.37	1.37
21	43530.5	ap^4G_4	1.27	1.27
22	44529.2	ap^4G_4	.97	.97
23	44797.4	ap^4F_5	1.33	1.33
24	45038.8	ap^4D_2	1.20	1.20
25	45988.5	ap^4G_3	.66	.57
26	46097.9	ap^4D_1	.00	.00
27	46163.7	ap^4F_4	1.18	1.24
28	47204.0	ap^2G_5	1.11	1.11
29	47267.0	ap^4F_3	.68	.40
30	47651.6	ap^2D_3	1.05	1.20
31	48031.4	ap^4F_3	1.04	1.03
32	48246.5	ap^2F_4	1.14	1.14
33	49237.7	ap^2G_4	.89	.89
34	50017.0	ap^2D_3	.86	.80
35	50672.6	ap^2F_3	1.16	.86
36	51673.5	bp^4P_3	1.33	1.73
37	51686.4	bp^4P_2	1.36	1.60
38	51726.4	bp^4P_1	2.25	2.67
39	53684.3	cp^2F_3	1.10	.86
40	54531.4	cp^2P_1	1.16	.67
41	54627.0	cp^2F_4	1.26	1.14
42	55875.1	cp^2P_2	1.16	1.33
43	56476.2	cp^2D_3	1.26	.80
44	56724.0	bp^4D_1	.07	.00
45	56976.0	cp^2D_2	1.25	1.20
46	57252.7	bp^4D_2	1.22	1.20
47	57369.0	bp^4D_3	1.30	1.37
48	57975.3	bp^4D_4	1.29	1.43
49	58708.7	kp^2H_5	.91	.91
50	58721.5	ep^2D_3	1.20	1.20
51	59291.3	ep^2D_2	.80	.80
52	59989.7	ep^2S_1	1.88	2.00
53	60070.0	ep^2P_2	1.50	1.33
54	60511.9	kp^2H_5	1.09	1.09
55	60962.1	kp^2F_3	1.14	1.14
56	61198.6	bp^4S_2	2.00	2.00
57	62039.4	kp^2F_3	.86	.86
58	62957.1	ep^2P_1	.70	.67
59	64601.5	kp^2G_4	.89	.89
60	64901.4	kp^2G_4	1.11	1.11
61	79532.8	$6s^4F_5$		
62	80224.6	$6s^4F_4$		
63	83062.9	$6s^2F_4$		
64	83064.3	$6s^4F_3$		
65	84246.5	$6s^4F_3$		
66	84845.6	$6s^2F_3$		
67	85122.2	$5d^4D_4$		
68	85804.0	$5d^4F_5$		
69	86007.5	$5d^4F_4$		
70	87791.7	$5d^4G_5$		
71	89856.5	$6s^4P_3$		
72	97621.8	$6s^2G_4$		

Intervals	
$4d^9D$	3539.
$5s^4F$	2013.3; 1832.7; 1018.6
^2F	2144.1
^4P	1083.5; 1137.4.
^2D	−1627.2
^2P	292.0
^2G	108.2
ap^4D	2715.2; 2157.6; 1059.1
^4F	1366.3; 1867.7; −764.4
^4G	−1312.5; 2311.2; 1459.3
^2D	2365.4
^2F	2426.1
^2G	2033.7
bp^4P	−12.9; 52.9
^4D	−606.3; −116.3; −528.7
cp^2P	−1343.7
^2D	−499.8
^2F	−942.7
ep^2P	2887.1
^2D	569.8
kp^2F	1077.3
^2G	−299.9
^2H	−1803.2
$6s^4F$	691.8; 2839.7; 1182.2
^2F	1782.7

Ionization Potential
$4d^9$ to $4d^8$ = 19.8 Volts
$4d^8 5s$ to $4d^8$ = 16.7 Volts

Terms	g-sums Obs.	g-sums Landé
$5s$		
$j=4$	3.33	3.27
$j=3$	4.79	4.69
$j=2$	4.32	4.26
$j=1$	3.42	3.34

Terms	g-sums Obs.	g-sums Landé
ap		
$j=4$	5.61	5.67
$j=3$	5.28	5.03
$j=2$	2.74	2.40
$j=1$	.00	.00

Terms	g-sums Obs.	g-sums Landé
bp, cp		
ep, kp		
$j=4$	4.58	4.60
$j=3$	7.07	7.09
$j=2$	9.27	9.19
$j=1$	6.01	6.06

[4] W. F. Meggers and Otto Laporte, Phys. Rev. **28**, 642 (1926).

The main criterion used in determining the nature of the terms was intensities, the large scale on which these were estimated by Dr. Meggers being particularly useful. In addition, however, Zeeman effects of the majority of the sharp lines were measured. They are discussed below.

In Table I are given the term values, taking the low term $5s\,^4F_5$ as zero. The lower term $4d^2D_3$ has not been taken as zero because of the fact that its

TABLE II. *Intensities in principle multiplets.*

	$5s\,^4F_5$	$^4F_4$	$^4F_3$	$^4F_2$	$^2F_4$	$^2F_3$
$ap\,^4D_4$	300	—	—		30	25
$^4D_3$		150	20	—	8	50
$^4D_2$			100	10		—
$^4D_1$				75		
$^4F_5$	100R	30			150	
$^4F_4$	10	40	50		150	30
$^4F_3$		20	30	10	80	40
$^4F_2$			10	40		70
$^4G_6$	200R					
$^4G_5$	75	250			200	
$^4G_4$	—	50	100		10	30
$^4G_3$		10	60	100	30	20
$^2D_3$		—	25	30	100	1
$^2D_2$			10	30		60
$^2F_4$	10	50	20		100	100
$^2F_3$		15	3	50	20	75
$^2G_5$	15	50			200	
$^2G_4$	—	7	30		20	150

value is based on the less accurately determined wave-lengths around λ1300. The intensities in the principal multiplets are shown in Table II. It will be seen that the intensity rules are reasonably satisfied, with the exceptions (1.) the entire absence of the line $5s\,^4F_4$–$ap\,^4D_4$, theoretically of intensity at least 20, and (2.) the rather large intensity of $5s\,^4F_3$–$ap\,^4F_4$. The term which has been taken as ap^2F_4 might have been interchanged with $ap\,^4F_4$ but for the fact that the combinations with $6s\,^4F$ settle the multiplicities unambiguously.

It will be noticed in Table I that the interval rule is not even approximately true in this spectrum. But it is very surprising that the term $ap\,^4F_2$ is lower than $ap\,^4F_3$. As far as intensities are concerned there is no choice between $ap\,^4F_2$ and ap^2D_2, but the intervals would be more anomalous if they were interchanged and in addition their Zeeman g's would be less in agreement with the Landé values.

ZEEMAN EFFECTS

The Zeeman patterns of the great majority of the sharp lines have been measured on plates taken with an Hilger E. 1 spectrograph. The magnetic field was about 34000 gauss and the times of exposure always less than an hour. Naturally, with such a spectrograph only wide patterns appear resolved, the remainder appearing as triplets, or as doublets in each polarization. The resolved patterns are given in Table III together with a few essential

unresolved triplets, but it has been considered unnecessary to reproduce the very large number of unresolved effects measured. The resolved patterns have made it possible to calculate some of the g-values with reasonable accuracy and such values are in italics in the term table. The remainder of the g-values were determined from the unresolved patterns by choosing

TABLE III. *Resolved Zeeman patterns of Pd II.*

	λ	$X-Y$	Z. E. Pattern	Approximate g_x	Approximate g_y	Remarks
1.	2488.41	$5s^4F_2-ap^4D_2$	O (−*1.20*) *0* .86? 1.63 C (−1.20) 0 *.80* 1.60	.40	1.20	Resolved completely
2.	2424.49	$5s^4F_2-ap^4D_1$	O (0) .56 C (.20) .20, .60	.40	0.0	
3.	2336.43	$5s^4F_2-ap^2D_3$	O (−.96)———*2.00* C (−.96)———*2.00*	.40	1.04	Resolved completely
4.	2315.87	$5s^4F_2-ap^4F_3$	O (−.93)———*1.99* C (−.93)———*1.99*	.44	1.06	Resolved completely
5.	2282.11	$5s^4F_3-ap^2D_3$	O (0) 1.06 C (0) 1.06	1.06	1.06	
6.	2262.52	$5s^4F_3-ap^4F_3$	O (0) 1.03 C (0) 1.03	1.03	1.03	
7.	2534.37	$5s^4P_2-bp^4P_1$	O (.39) *1.07* 1.86 C (.39) *1.08* 1.86	1.47	2.25	
8.	2731.80	$5s^4P_1-ap^2D_2$	O (.93) *0* C (.93) *.07* 1.79	2.72	.86	
9.	2613.42	$5s^4P_1-bp^4P_2$	O (.65) *.68* C (.68) *.68* 2.04	2.63	1.33	Very faint pattern
10.	2431.78	$5s^4P_1-cp^2P_1$	O (.80) 1.96 C (.80) 1.96	2.76	1.16	Very faint pattern
11.	2354.76	$5s^4P_1-cp^2P_2$	O (.78) *.39* 1.97 C (.78) *.38* 1.94	2.76	1.16	
12.	2321.91	$5s^4P_1-cp^2D_2$	O (.75) *.50* 2.01 C (.75) .51 2.01	2.76	1.26	
13.	2308.60	$5s^4P_1-bp^4D_1$	O (1.34) 1.41 C (1.34) 1.41	2.75	.07	
14.	2280.79	$5s^4P_1-bp^4D_2$	O (.74) *.47* 1.96 C (.74) *.48* 1.96	2.70	1.22	
15.	2637.08	$5s^2P_2-cp^2D_2$	O (0) 1.25 C (0) 1.25	1.25	1.25	
16.	2602.76	$5s^2P_2-cp^2D_3$	O (0) 1.24 C (0) 1.24	1.24	1.24	
17.	2413.37	$5s^2P_2-ep^2S_1$	O (.30) *.95*— C (.30) *.95* 1.55	1.25	1.85	
18.	2430.53	$5s^2P_1-ep^2S_1$	O (.62) 1.28 C (.62) 1.28	.66	1.90	
19.	2425.78	$5s^2P_1-ep^2P_2$	O (.39) 1.14 *1.89* C (.39) 1.11 *1.89*	.72	1.50	
20.	2266.96	$5s^2P_1-ep^2P_1$	O (0) .70 C (0) .70	.70	.70	Very faint
21.	2433.11	$5s^2G_5-kp^2H_6$	O (0) 1.07 C (0) 1.05 (Blend)	1.11	1.09	
22.	2218.15	$5s^2G_4-kp^2G_4$	O (0) .93 C (0) .89	.89	.89	
23.	2330.05	$5s^2S_1-{}^2P_1$?	O (.70) 1.36 C (.67) 1.33	2.00	.67	Unplaced line

such values as would fit all the combinations of a given term most closely. The resulting g's are, of course, inaccurate; but, in cases where a large number of combinations occur they should not be in error by more than 5 percent. The pattern of every line measured is consistent with the G's calculated.

An examination of the g's given in the term table shows at once how far from regular this spectrum is. Amongst the low terms, $5s^2F_3$ and $5s^2D_2$ have exceptionally high values, whereas $5s^4P_3$ and $5s^4P_2$ have very low ones. The outstanding features in the ap triad are the very high g-values for ap^4F_2 and ap^2F_3. With the term table there is also given a comparison of the sums of the observed g's with the g-sums obtained from Landé's values. The agreement is excellent except in two cases in the ap triad.

The triads associated with the low $5s^4P$, ^2P, ^2D, ^2G are all overlapping in the region of terms between 51000 and 65000. By considering the intensities and the Zeeman effects for this group of terms, it is possible to assign designations to all of them with considerable certainty. They then fall naturally into groups which, from the fact that they combine most strongly with one or another of the low terms, evidently belong together. Table IV shows this grouping.

TABLE IV. *Origin of Terms of Pd II.*

Pd III Config.	Pd III Term	Added Electron	Terms Theoretical	Terms Empirical
$4d^8$	All	$4d$	^2D	$4d^2D$
	^3F	$5s$	$^4\&^2F$	$5s^4\&^2F$
		$5p$	$^4\&^2D, F, G$	$ap^4\&^2D, F, G$
		$6s$	$^4\&^2F$	$6s^4\&^2F$
		$5d$	$^4\&^2P, D, F, G, H.$	$5d^4D, F, G,$ (Parts of)
	^3P	$5s$	$^4\&^2P$	$5s^4\&^2P$
		$5p$	$^4\&^2S, P, D.$	$bp^4S, P, D.$ $ep^2S, P, D.$
		$6s$	$^4\&^2P$	$6s^4P_3$
	^1S	$5s$	^2S	Possibly
		$5p$	^2P	present
	^1D	$5s$	^2D	$5s^2D$
		$5p$	$^2P, D, F$	$cp^2P, D, F.$
	^1G	$5s$	^2G	$5s^2G.$
		$5p$	$^2F, G, H.$	$kp^2F, G, H.$
		$6s$	^2G	$6s^2G_5$

The extreme irregularity of the intervals and g's should be noted. bp^4P is very narrow and bp^4D is completely inverted; the kp group contains both positive and negative intervals.

THE LOW ^{2}D TERM

The lowest term of Pd II should theoretically be the ^2D arising from the structure $4d^9$. Since this term is now known in Ni II[2] a prediction of its position in Pd II can be made from the relative change in the equivalent $^1S(d^{10})$ between the spectra Cu II[3] and Ag II.[5] The prediction places the ^2D term about 25500 below $5s^4F_5$, which would bring its strong combinations with the ap triad about λ1400. The term is actually found to have the values $-25081(j=3)$ and $-21542(j=2)$ and gives 51 lines in combination

[5] A. G. Shenstone, Phys. Rev. 31, 317 (1928).

with the terms of the structure $4d^8 5p$. This $4d^2D$ term was found by Mr. H. E. White, of Cornell University, from his own measurements and the values of the $5p$-terms found by the author. The term combines indiscriminately with quartet and doublet terms as is the case also in Rh I.[6] The strongest lines are produced in combination with ap^2D, the ap^2F lines being unexpectedly weak.

In a recent letter to "Nature"[7] the author has pointed out that there are three complete series members of the $^3D^1D(d^9s)$ series of Pd I. The third member of this series includes McLennan and Smith's term a^3G_4 as $^3D_3$, the remainder being their 3^3D & ^1D with the $^1D_2$ and $^3D_2$ interchanged. The series of $^3D_3$ and $^3D_1$ terms have as limits the 4^2D_3 & 4^2D_2 terms of Pd II. As in all other series of this type, the separation $^3D_3 - {}^3D_1$ is practically constant and equal to $^2D_3 - {}^2D_2$. The term differences in the present case are as follows:

1st member	$(^3D_2 - {}^3D_1) = 3529.9$
2nd member	$(^3D_2 - {}^3D_1) = 3532.1$
3rd member	$(^3D_2 - {}^3D_1) = 3538.7$
Limit Pd II	$(^2D_3 - {}^2D_2) = 3539.$

Missing Terms

Table I includes all the terms predicted by the Hund theory for the assumed structures, with the following exceptions: (1) a $^2S_1$ from $4d^8 5s$, and (2) the $^2P(4d^8 5p)$ which forms the whole triad connected with that ^2S. There are just five lines of Class 1 which remain unaccounted for by the terms of Table I. Of these lines λ2430.05 (2) has the Zeeman pattern characteristic of $^2S_1 - {}^2P_1$ and λ2322.59 (5) a pattern which could be that of $^2S_1 - {}^2P_2$. All attempts to connect these lines with the rest of the spectrum have failed because of the paucity of combinations. It should be noted that neither the terms in question, nor the $^1S(d^8)$ on which they are built, have been identified in any spectrum, as far as the author is aware.

Diffuse Lines

The spectrum contains a very large number of diffuse lines which must be produced by combinations of the middle terms with high terms from the structures $4d^8 6s$ and $4d^8 5d$. All the most intense are accounted for by the former structure which gives the terms $6s^{4\&2}F$. Some search has been made for other high terms and a few are given in the term table as identified. Undoubtedly, a great many more could be found, but the inaccuracy of the measurements of the diffuse lines is so great that it is frequently difficult to be sure of the reality of a term.

In Table V are given all the identified lines of the spectrum. The five unidentified lines, mentioned above, have also been included.

[6] L. A. Sommer, Zeits. f. Physik **45**, 147 (1927).
[7] A. G. Shenstone, Nature **121**, 619 (1928).

TABLE V. *Classified lines of the palladium spark spectrum.*

λ	Auth.	Int.	ν	Combination
4156.95	E	1	24049.3	$5s^2D_3-ap^4D_4$
3999.46	E	1	24996.3	$5s^2G_4-ap^4G_5$
3982.25	E	1	25104.4	$5s^2G_3-ap^4G_4$
3818.70	E	1	26179.5	$5s^2P_1-ap^4D_2$
3778.83	E	1	26455.7	$5s^2G_4-ap^4G_5$
3738.84	E	6	26738.7	$5s^2G_3-ap^4F_4$
3735.36	E	1	26763.6	$5s^2D_3-ap^4D_3$
3670.12	E	1	27239.3	$5s^2P_1-ap^4D_1$
3598.72	E	1	27779.8	$5s^2G_3-ap^4G_3$
3555.33	E	1	28118.8	$5s^2G_4-ap^2D_3$
3507.95	E	7A	28498.6	$5s^2G_4-ap^4F_5$
3468.57	E	8A	28822.1	$5s^2G_3-ap^2F_4$
3451.37	E	20A	28965.7	$5s^4P_3-ap^4D_4$
3382.90	E	1	29552.0	$ap^2F_3-6s^4F_4$
3353.36	E	4A	29812.3	$5s^2G_3-ap^2G_4$
3346.77	E	2A	29871.0	$5s^2D_3-ap^4G_3$
3327.23	E	10A	30046.4	$5s^2D_3-ap^4F_4$
3272.56	E	10A	30548.3	$5s^2D_3-ap^4D_3$
3267.36	E	30A	30597.0	$5s^4P_3-ap^4D_3$
3243.13	E	25A	30825.5	$5s^2F_3-ap^4D_4$
3210.43	E	10A	31139.5	$5s^2G_4-ap^2F_3$
3209.42	E	2A	31149.3	$5s^2D_3-ap^4F_3$
3178.77	E	5A	31449.6	$5s^2P_1-ap^2D_2$
3173.88	E	2A	31498.1	$5s^2D_3-ap^4G_3$
3170.26	E	20A	31534.1	$5s^2D_3-ap^2D_3$
3162.86	E	4A	31607.8	$5s^2D_3-ap^4D_2$
61.95	E	25A	31616.9	$5s^4P_1-ap^4D_2$
55.59	E	15A	31680.7	$5s^4P_2-ap^4D_3$
35.78	S	10ua	31880.8	$bp^4D_4-6s^4P_3$
32.49	E	10A	31914.3	$5s^2D_3-ap^4F_3$
11.53	E	2A	32129.2	$5s^2D_3-ap^2F_4$
09.16	E	7A	32153.6	$5s^2G_4-bp^4P_3$
3105.33	E	8ua	32193.4	$ap^4F_3-6s^4F_4$
3086.53	S	3u	32389.5	$ap^2F_3-6s^2F_4$
69.2	E	3ua	32572.3	$ap^2D_3-6s^4F_4$ $bp^4P_3-6s^4F_3$
59.43	E	25A	32676.3	$5s^4P_3-ap^4D_3$
55.3	E	10ua	32720.5	$kp^2G_4-6s^2G_4$
52.14	E	20A	32754.4	$5s^4P_3-ap^4D_2$
50.06	E	10A	32776.7	$5s^2D_3-ap^4F_3$
46.49	E	2A	32815.1	$5s^2P_1-bp^4P_2$
41.66	E	8A	32867.2	$5s^2P_1-bp^4P_1$
32.20	E	30A	32969.8	$5s^2F_4-ap^4D_4$
19.63	E	7A	33107.0	$5s^2P_2-bp^4P_2$
18.47	E	8A	33119.8	$5s^2D_3-ap^2G_4$ $5s^2P_2-bp^4P_2$
15.06	S	5ua	33157.2	$bp^4P_2-6s^2F_3$?
3013.90	S	5ua	33170.0	$bp^4P_3-6s^2F_3$?
2999.55	E	40A	33328.7	$5s^4P_3-ap^4G_4$
80.63	E	50A	33540.2	$5s^2F_3-ap^4D_3$ $5s^2D_3-ap^4F_3$
2956.48	E	8A	33814.2	$5s^4P_2-ap^4D_2$
55.53	S	2ua	33825.0	$ap^2G_4-6s^2F_4$
54.37	E	15A	33838.3	$5s^4P_3-ap^4D_3$
53.78	E	2A	33845.1	$5s^4P_1-ap^4F_2$
49.09	E	3A	33898.9	$5s^2D_3-ap^2D_2$
35.01	E	20ua	34061.5	$ap^4F_4-6s^4F_4$
27.25	E	8A	34151.8	$5s^2G_4-cp^2F_3$
25.41	E	10ua	34173.3	$ap^2F_3-6s^2F_3$
2920.6	E	5ua	34229.5	$ap^2D_3-6s^4F_3$
2893.09	E	10A	34555.0	$5s^2D_3-ap^2F_3$
78.01	E	100ua	34736.1	$ap^4F_4-6s^4F_4$
71.37	E	100ua	34816.4	$ap^2F_4-6s^2F_4$
70.4	E	1ua	34828.2	$ap^2D_3-6s^2F_3$
59.29	E	8A	34963.5	$5s^4P_3-ap^4F_4$
57.70	E	20A	34982.9	$5s^4P_3-ap^4F_3$
54.59	E	200A	35021.0	$5s^2F_4-ap^4G_5$
53.64	E	10ua	35032.7	$ap^4F_3-6s^4F_3$
46.74	E	10A	35117.6	$5s^2P_2-cp^2F_3$
41.02	E	30A	35188.3	$5s^2F_3-ap^4G_4$
39.89	E	20A	35202.3	$5s^2G_4-cp^2F_4$
37.64	E	20ua	35230.2	$cp^2F_4-6s^4P_3$
29.2	E	5ua	35335.3	$ap^2F_3-5d^4F_4$
23.1	E	10ua	35411.7	$ap^2D_3-6s^2F_4$
21.91	E	30ua	35426.6	$ap^4F_4-6s^4F_4$
13.98	E	10A	35526.4	$5s^2D_3-ap^2D_3$
11.59	E	3A	35556.6	$5s^2D_3-bp^4P_2$
07.59	E	50ua	35607.3	$ap^2G_4-6s^2F_3$
02.46	E	10A	35672.4	$5s^2P_1-cp^2P_1$
01.54	E	8A	35684.2	$5s^2F_4-ap^4D_3$
2800.64	E	50ua	35695.6	$ap^4G_4-6s^4F_4$
2796.62	E	3A	35746.9	$5s^4P_3-ap^4F_3$
87.92	E	100ua	35858.5	$ap^2G_4-6s^2F_4$
79.69	E	5A	35964.6	$5s^2P_2-cp^2P_1$
76.85	E	150ua	36001.4	$ap^4G_4-6s^4F_4$
71.88	E	5A	36066.0	$5s^4P_2-ap^4F_3$
42.57	E	25A	36451.4	$5s^4P_2-ap^2D_3$
2731.80	E	15A	36595.1	$5s^4P_1-ap^2D_2$
27.82	E	20A	36647.4	$5s^2F_3-ap^4G_3$
26.92	E	5ua	36660.6	$kp^2F_4-6s^2G_3$
14.89	E	30A	36823.0	$5s^2F_3-ap^4F_4$
14.30	E	15A	36831.0	$5s^4P_2-ap^4F_3$
09.15	E	15ua	36901.0	$ap^4F_4-6s^4F_3$
2703.37	E	5ua	36979.8	$ap^4F_3-6s^4F_3$
2698.53	E	25A	37046.2	$5s^4P_2-ap^2F_4$
96.4	E	5ua	37075.5	$ap^4G_3-6s^4F_3$
93.9	E	10ua	37109.9	$kp^2H_4-6s^2G_3$
88.53	E	20A	37184.0	$5s^2D_3-bp^4P_2$
87.65	E	20A	37196.2	$5s^2D_3-bp^4P_3$
84.77	E	8A	37236.1	$5s^2D_3-bp^4P_1$
79.59	E	12A	37308.1	$5s^2P_2-cp^2P_2$
79.10	E	5ua	37314.9	$ap^4G_3-6s^4F_3$
77.86	E	10A	37332.2	$5s^2F_4-ap^4G_4$
77.05	E	5ua	37343.5	$ap^4D_3-6s^4F_4$
69.95	E	1	37442.8	$5s^2G_4-cp^2D_3$
61.15	E	10A	37566.6	$5s^2D_3-cp^2F_3$
60.3	E	1u	37578.6	$ap^4F_3-6s^2F_3$
58.75	E	150A	37600.5	$5s^2F_4-ap^4F_3$
57.58	E	25A	37617.0	$5s^2P_1-cp^2D_2$
49.48	E	20A	37732.0	$5s^4P_3-ap^2D_3$
42.20	E	12A	37836.0	$5s^2G_4-bp^4D_3$
40.18	E	5A	37865.0	$5s^2P_1-bp^4D_1$
37.08	E	15A	37909.5	$5s^2P_2-cp^2D_3$
35.92	E	70A	37926.1	$5s^2F_3-ap^4F_3$
32.45	E	2u	37976.1	$ap^4F_3-5d^4F_4$
30.30	E	20ua	38007.2	$ap^4G_3-6s^4F_4$
29.00	E	5ua	38026.0	$ap^4D_3-6s^4F_3$
28.24	E	50A	38037.0	$5s^4P_3-ap^2G_4$
20.56	E	2ua	38148.4	$ap^4D_3-6s^4F_3$
19.07	E	4ua	38170.1	$bp^4P_3-6s^4F_4$
18.22	E	2ua	38182.5	$bp^4P_3-6s^4P_3$
13.42	E	20A	38252.6	$5s^4P_1-bp^4P_2$
13.15	S	4ua	38256.5	$ap^4G_3-6s^4F_3$
09.85	E	8A	38305.0	$5s^4P_1-bp^4P_1$
09.49	M	1	38310.9	$5s^2F_3-ap^2D_3$
06.36	E	2ua	38356.2	$ap^2D_3-5d^4F_4$
03.82	M	1A	38393.7	$5s^2P_1-bp^4D_2$
2002.76	E	35A	38409.3	$5s^2P_2-cp^2D_3$
2595.98	E	40A	38509.6	$5s^2D_3-cp^2F_4$
94.3	E	10ua	38534.3	$ap^4G_4-6s^4F_3$
93.24	E	60A	38550.3	$5s^2G_4-bp^4D_4$
89.70	S	1u	38602.9	$ap^2G_4-5d^4F_4$
84.13	E	5A	38686.2	$5s^2P_3-bp^4D_3$
83.84	E	40A	38690.5	$5s^2F_3-ap^4F_3$
77.08	E	30A	38792.0	$5s^2F_4-ap^4G_5$
76.39	E	15A	38802.4	$5s^2P_3-bp^4D_3$
75.46	E	10A	38816.4	$5s^4P_3-ap^2D_3$
72.7	E	1ua	38858.0	$ap^4G_3-6s^2F_3$
69.56	E	100A	38905.5	$5s^2F_3-ap^2F_4$
65.51	E	150A	38966.9	$5s^2F_4-ap^4F_4$
61.02	E	20A	39035.2	$5s^4F_3-ap^4D_3$
51.84	E	150A	39175.7	$5s^2G_4-kp^2H_5$
51.01	E	8A	39188.4	$5s^2G_4-ep^2D_3$
50.64	E	40A	39194.1	$5s^2D_3-cp^2F_3$
44.82	E	25A	39283.7	$5s^2G_3-kp^2H_4$
39.44	E	50ua	39367.0	$ap^4D_4-6s^4F_3$
37.94	E	8A	39390.2	$5s^4P_3-bp^4P_3$
37.13	E	10A	39403.8	$5s^4P_3-bp^4P_2$
34.57	E	80A	39442.6	$5s^4P_3-bp^4P_1$
32.66	E	1A	39472.3	$5s^4P_3-ap^2F_3$
21.86	E	4ua	39641.3	$ap^4F_4-5d^4F_4$
21.49	E	2u	39647.2	$bp^4D_3-6s^2G_4$
14.47	E	50A	39757.8	$5s^2D_3-cp^2P_2$
09.11	E	10ua	39842.8	$ap^4F_4-5d^4F_4$
2505.73	E	150A	39896.5	$5s^2F_3-ap^2G_4$
2498.81	E	200A	40007.0	$5s^2F_4-ap^2G_4$
96.72	E	40A	40040.5	$5s^2D_3-cp^2P_1$
89.61	E	75A	40154.8	$5s^2P_3-ep^2D_3$
88.92	E	300A	40166.0	$5s^4F_4-ap^4D_4$
88.41	E	10A	40174.2	$5s^4F_3-ap^4D_3$
86.52	E	250A	40204.7	$5s^4F_4-ap^4G_5$
79.11	E	20ua	40324.9	$ap^4F_3-5d^4D_4$
77.02	E	15A	40358.9	$5s^2D_3-cp^2D_3$
72.55	E	50A	40431.9	$5s^2P_1-ep^2D_2$
71.18	E	100A	40454.3	$5s^2F_4-ap^2D_3$
70.06	E	80A	40472.6	$5s^4P_3-bp^4P_2$
69.29	E	150A	40485.2	$5s^4P_3-bp^4P_3$
57.76	E	60A	40675.1	$5s^2F_3-ap^2D_2$
57.29	E	100A	40682.9	$5s^4F_3-ap^4G_4$
54.75	E	30A	40725.0	$5s^2P_3-ep^2D_3$
48.15	E	80A	40834.7	$5s^2F_4-ap^4F_4$
46.72	E	75A	40858.7	$5s^2D_3-cp^2D_3$
46.17	E	150A	40867.8	$5s^4F_4-ap^4D_3$
37.89	E	10ua	41006.6	$ap^4F_3-5d^4F_4$

TABLE V. (continued)

λ	Auth.	Int.	ν	Combination
2435.32	E	100A	41049.9	$5s^2F_4-ap^2F_5$
33.14	E	100A	41087.2	$5s^2G_4-kp^2H_5$
31.78	E	3A	41109.7	$5s^4P_3-cp^2P_3$
30.94	E	100A	41123.9	$5s^4F_3-ap^4G_3$
30.53	E	10A	41130.8	$5s^2P_1-ep^2S_1$
30.27	E	2A	41135.2	$5s^2D_3-bp^4D_3$
30.05	E	2A	41139.2	$5s^2S_1-{}^3P_1$?
26.87	E	100A	41192.8	$5s^4F_3-ap^4D_2$
25.78	E	10A	41211.3	$5s^2P_1-ep^2P_1$
24.49	E	75A	41233.3	$5s^4F_2-ap^4D_1$
23.42	E	2A	41251.5	$5s^2D_3-bp^4D_3$
22.09	E	2ua	41274.1	$ap^4G_4-5d^4F_4$
18.72	E	75A	41331.6	$5s^2F_3-ap^2F_3$
16.67	E	6ua	41366.7	$ap^4D_3-6s^4F_2$?
15.62	E	15A	41384.7	$5s^2D_3-cp^2P_3$
14.73	E	60A	41399.9	$5s^4P_3-cp^2F_3$
13.37	E	10A	41423.2	$5s^2P_1-ep^2S_1$
10.15	E	5ua	41478.6	$ap^4G_4-5d^4F_4$
08.71	E	20A	41503.4	$5s^2P_3-ep^2P_3$
06.75	E	40A	41537.2	$5s^2G_4-kp^2F_4$
01.47	E	30ua	41628.5	$ap^4F_4-5d^4G_5$
88.29	E	50A	41858.2	$5s^2D_3-bp^4D_3$
81.99	S	1A Fe?	41968.9	unidentified
81.02	E	1A	41986.0	$5s^2D_3-cp^2D_2$
77.90	E	20A	42041.1	$5s^2F_4-ap^2G_4$
72.16	E	60A	42142.8	$5s^4F_3-ap^4G_3$
67.92	E	75A	42218.2	$5s^4F_4-ap^4G_5$
67.00	E	2A	42234.7	$5s^2D_3-bp^4D_3$
66.27	E	2A	42247.7	$5s^4P_3-cp^2P_3$
64.79	E	3ua	42274.1	$ap^4G_4-5d^4F_4$
62.31	E	50A	42318.5	$5s^4F_4-ap^4F_4$
61.47	E	4A	42333.6	unidentified
61.14	E	2A	42339.5	$5s^2P_1-bp^4S_2$
57.61	E	40A	42402.9	$5s^4F_3-ap^4F_3$
54.76	E	8A	42454.2	$5s^4P_1-cp^2P_2$
52.99	E	1A	42487.1	$5s^2D_-cp^2D_3$
51.85	E	25A	42506.7	$5s^2G_4-kp^2F_4$
51.32	E	50A	42516.3	$5s^4F_4-ap^4G_4$
47.52	E	5A	42585.2	unidentified
47.26	E	8ua	42589.8	$ap^4F_3-6s^4P_2$?
46.46	E	7A	42604.3	$5s^2D_3-ep^2D_3$
44.95	E	3A	42631.8	$5s^2P_3-bp^4S_2$
37.75	E	15A	42763.0	$5s^2D_3-bp^4D_3$
36.59	E	30A	42784.3	$5s^4F_4-ap^4F_4$
36.43	E	30A	42787.2	$5s^4F_3-ap^2D_3$
31.41	E	30A	42879.3	$5s^2D_3-bp^4D_3$
30.0	E	3ua	42905.3	$ap^4G_5-5d^4D_4$
25.2	E	3ua	42993.8	$ap^4F_4-5d^4G_5$ $cp^2F_4-6s^2G_4$
22.59	E	5A	43042.1	unidentified
21.91	E	8A	43054.7	$5s^4P_1-cp^2D_2$
18.07	E	2ua	43126.1	$ap^4D_3-5d^4F_4$
15.87	E	10A	43167.0	$5s^4F_3-ap^4F_3$
08.60	E	10A	43302.9	$5s^4P_1-bp^4D_1$
02.35	E	10A	43420.5	$5s^4F_3-ap^4F_3$
2302.02	E	40A	43426.7	$5s^4P_3-cp^2F_4$
2299.58	E	5A	43472.7	$5s^2P_3-kp^2F_4$
99.43	E	20A	43475.6	$5s^2F_4-ap^2F_3$
96.53	E	200RA	43530.5	$5s^4F_3-ap^4G_4$
93.71	E	5ua	43584.0	$ap^4G_4-5d^4F_5$
93.35	E	8A	43590.9	$5s^2P_3-cp^2P_3$
82.98	E	3u	43788.9	$ap^4G_5-5d^4F_4$
82.11	E	25A	43805.5	$5s^4F_4-ap^2D_3$
80.79	E	15A	43830.9	$5s^4P_1-bp^4D_2$
74.47	E	8A	43952.7	$5s^2D_3-ep^2P_2$
73.34	E	10A	43974.5	$5s^4F_4-ap^4G_5$
66.96	E	8A	44098.3	$5s^2P_1-ep^2P_1$
64.33	E	40A	44149.5	$5s^4F_4-ap^4F_4$
62.52	E	30A	44184.8	$5s^4F_3-ap^4F_3$
62.15	E	15A	44192.0	$5s^4P_3-cp^2D_3$
60.13	E	5A	44231.5	$5s^2D_3-ep^2D_3$
54.45	S	3A	44343.0	$5s^2F_3-cp^2F_3$
52.04	S	20A	44390.4	$5s^2P_3-ep^2P_3$
51.51	S	20A	44400.8	$5s^4F_3-ap^2F_4$
49.52	S	3A	44440.0	$5s^4P_2-bp^4D_2$
47.00	S	1A	44489.9	$5s^2F_4-bp^4P_3$
37.72	S	5A	44674.5	$5s^4P_3-cp^2P_3$
36.84	S	3A	44692.1	$5s^4P_3-cp^2D_3$
31.59	S	100RA	44797.2	$5s^4F_3-ap^4F_3$
29.22	S	25A	44844.8	$5s^2D_3-kp^2F_4$
23.75	S	25ua	44955.1	$ap^4D_4-5d^4D_5$
23.06	S	3A	44968.9	$5s^4P_3-bp^4D_3$
18.15	S	30A	45068.6	$5s^2G_4-kp^2G_4$?
17.53	S	15A	45081.2	$5s^2D_3-bp^4S_2$
17.32	S	10A	45085.4	$5s^4P_3-bp^4D_3$
14.03	S	30A	45152.3	$5s^4F_3-ap^2D_3$
12.15	S	50A	45190.8	$5s^4F_4-ap^2G_5$
2207.97	S	0	45276.2	$5s^4P_3-cp^2D_3$
07.47	S	25A	45286.1	$5s^2F_3-cp^2F_4$
03.48	S	10A	45368.5	$5s^2G_4-kp^2G_5$
2202.36	S	30A	45391.7	$5s^4F_4-ap^2G_5$
2198.24	S	30A	45476.7	$5s^2G_4-kp^2G_5$
97.14	S	2A	45499.5	$5s^2D_2-ep^2S_1$
94.56	S	3u	45573.7	$ap^4G_5-5d^4G_5$
93.27	S	3A	45579.7	$5s^2D_3-ep^2P_2$
90.53	S	10ua	45636.7	$ap^4D_4-5d^4F_4$
82.35	S	50A	45807.8	$5s^4F_3-ap^2F_3$
80.80	S	0u	45840.3	$ap^4D_4-5d^4F_4$
79.41	S	5A	45869.6	$5s^4P_1-ep^2D_2$
76.91	S	25a	45922.2	$5s^2D_3-kp^2F_3$?
72.38	S	20A	46018.0	$5s^4F_4-ap^4F_5$
70.76	S	1	46052.3	$5s^4P_3-bp^4D_3$
65.50	S	10A	46163.0	$5s^4F_4-ap^4F_4$
65.30	S	5A	46168.4	$5s^4P_3-bp^4D_3$
65.20	S	10A	46170.7	$5s^4F_3-ap^2D_2$
62.27	S	50A	46233.1	$5s^4F_4-ap^2F_4$
52.76	S	30A	46437.3	$5s^4P_3-ep^2D_3$
48.27	S	15A	46534.4	$5s^2F_3-cp^2P_2$
46.69	S	3A	46568.3	$5s^4P_1-ep^2S_1$
41.36	S	5A	46648.6	$5s^4P_1-ep^2P_2$
40.26	S	20A	46708.4	$5s^2D_3-bp^4S_2$
37.26	S	20A	46774.6	$5s^4P_3-bp^4D_3$
35.64	S	8A	46809.6	$5s^4F_3-bp^4P_3$
35.07	S	10A	46822.1	$5s^4F_3-bp^4P_2$
34.85	S	3A	46826.9	$5s^4F_3-ap^2F_3$
33.25	S	0	46862.0	$5s^4F_3-bp^4P_2$
26.64	S	10A	47007.5	$5s^4P_3-ep^2D_3$
20.85	S	1A ?	47135.9	$5s^2F_3-cp^2D_3$
17.80	S	5A	47203.9	$5s^4F_3-ap^2G_4$
16.88	S	7A	47224.4	$5s^4F_4-ap^2G_4$
07.69	S	3A	47430.2	$5s^2F_4-cp^2F_4$
03.67	S	10A	47520.8	$5s^4P_3-ep^2D_3$
2102.43	S	10A	47548.8	$5s^2D_3-kp^2F_3$
2098.64	S	5A	47634.7	$5s^2F_3-cp^2D_3$
95.54	S	5A	47705.2	$5s^4P_3-ep^2S_1$
92.39	S	15A	47776.9	$5s^4P_1-bp^4S_2$
92.01	S	15A	47785.7	$5s^4P_3-ep^2P_3$
90.17	S	8A	47827.7	$5s^4F_3-bp^4P_2$
89.61	S	10A	47840.6	$5s^4F_3-bp^4P_3$
86.50	S	12A	47911.9	$5s^2F_3-bp^4D_3$
81.43	S	10A	48028.6	$5s^2F_3-bp^4D_3$
72.05	S	10A	48245.9	$5s^4F_3-ap^2F_4$
62.60	S	3A	48467.0	$5s^2D_3-ep^2P_3$
55.51	S	1A	48634.0	$5s^2F_3-bp^4D_4$
54.46	S	15A	48659.0	$5s^4F_4-ap^2F_3$
45.62	S	10A	48869.2	$5s^4P_3-ep^2P_3$
43.79	S	8A	48913.0	$5s^4P_3-bp^4S_2$
08.21	S	8A	49779.4	$5s^2F_4-cp^2D_3$
λ (vac.)				
2000.07	S	8A	49998.3	$5s^4P_3-bp^4S_2$
1971.27	S	0 ?	50728.8	$5s^2F_3-ep^2P_3$
1552.19	W	3	64425	$4d^2D_3-ap^4D_3$
1532.81	W	6 ?	65240	$4d^2D_3-ap^4D_4$
1480.78	W	1 ?	67532	$4d^2D_3-ap^4G_4$
78.42	W	1	67640	$4d^2D_3-ap^4D_3$
71.34	W	5	67965	$4d^2D_3-ap^4D_3$
53.25	W	10	68811	$4d^2D_3-ap^4F_4$
45.20	W	5	69195	$4d^2D_3-ap^2D_3$
37.29	W	30	69575	$4d^2D_3-ap^4F_4$
36.53	W	3	69612	$4d^2D_3-ap^4G_4$
26.10	W	3 ?	70121	$4d^2D_3-ap^4D_3$
07.06	W	5	71070	$4d^2D_3-ap^4G_5$
1403.59	W	25	71246	$4d^2D_3-ap^4F_4$
1397.46	W	15	71558	$4d^2D_3-ap^2D_3$
84.79	W	3	72213	$4d^2D_3-ap^2F_3$
82.23	W	3	72347	$4d^2D_3-ap^4F_3$
74.92	W	50	72732	$4d^2D_3-ap^2D_3$
67.76	W	25	73112	$4d^2D_3-ap^4F_3$
65.80	W	25	73217	$4d^2D_3-bp^4P_3$
65.58	W	15	73229	$4d^2D_3-bp^4P_3$
64.81	W	1	73270	$4d^2D_3-bp^4P_2$
63.76	W	20	73327	$4d^2D_3-ap^2F_4$
15.57	W	25	74318	$4d^2D_3-ap^2G_4$
01.61	W	5	75097	$4d^2D_3-ap^2D_2$
00.34	W	5	75225	$4d^2D_3-cp^2F_3$
00.05	W	35	75754	$4d^2D_3-ap^2F_3$
14.61	W	5	76068	$4d^2D_3-cp^2P_3$?
02.85	W	7	76755	$4d^2D_3-bp^4P_3$
1302.66	W	8	76766	$4d^2D_3-bp^4P_3$
1281.79	W	1	78017	$4d^2D_3-cp^2D_3$
73.60	W	10	78518	$4d^2D_3-cp^2D_3$
69.62	W	10	78764	$4d^2D_3-cp^2F_3$
67.27	W	10	78910	$4d^2D_3-bp^4D_3$
54.59	W	20	79707	$4d^2D_3-cp^2F_3$

TABLE V. (continued)

λ	Auth.	Int.	ν	Combination	λ	Auth.	Int.	ν	Combination
1245.92	W	5	80262	$4d^2D_3-ep^2D_3$	1208.68	W	5d	82735	$4d^2D_3-bp^4S_2$
37.12	W	15	80833	$4d^2D_3-ep^2D_2$	04.00	W	30	83057	$4d^2D_3-bp^4D_4$
35.23	W	15	80957	$4d^2D_3-cp^2P_2$	1196.43	W	10	83582	$4d^2D_3-kp^2F_3$
26.54	W	5	81530	$4d^2D_3-ep^2S_1$	85.27	W	1	84369	$4d^2D_3-ep^2D_3$
26.19	W	1	81553	$4d^2D_1-cp^2D_2$	83.45	W	20	84499	$4d^2D_1-ep^2P_1$
25.33	W	10	81611	$4d^2D_3-ep^2P_2$	74.37	W	20	85152	$4d^2D_3-ep^2P_2$
18.66	W	15	82057	$4d^2D_3-cp^2D_3$	62.20	W	15	86044	$4d^2D_3-kp^2F_4$
14.58	W	10	82333	$4d^2D_3-bp^4D_3$	59.05	W	10	89278	$4d^2D_3-bp^4S_2$
12.88	W	3	82448	$4d^2D_3-bp^4D_2$	1115.16	W	1	89673	$4d^2D_3-kp^2G_4$?

E. Exner and Haschek.
S. Author.
W. Communication from H. E. White.
M. Communication from W. F. Meggers.
R. Reversed.
u. Diffuse
A. Relatively strong in the arc.
a. Relatively weak in the arc, but present.

LIMITS AND IONIZATION POTENTIAL

The identification of the $6s^{4\&2}F$ terms allows an approximate calculation of the series limits to be made. Theoretically, the limits should coincide in pairs $^4F_5$, $^2F_4$; $^4F_4$, $^2F_3$; $^4F_3$, $^4F_2$. There is, however, no indication of such a grouping in the calculated limits which are as follows:

Limit $^4F_5$	135524	Limit $^4F_2$	140185
$^4F_4$	135765	$^2F_4$	137713
$^4F_3$	139006	$^2F_3$	139329

It seems more probable that the $^4F_5$ and $^4F_4$, instead of $^2F_4$, limits coincide. This is another indication that the Hund theory of limits yields erroneous results for spectra of which the nature is determined by nearly completed electron groups. More definite evidence has been recently given by the author in the letter to Nature before mentioned.

The limit for the $^4F_5$ series can, however, be used to calculate an approximate ionization potential of 16.7 volts from $4d^85s$ to $4d^3$ or 19.8 volts from $4d^9$ to $4d^8$.

COMPARISON WITH SIMILAR SPECTRA

There are three analyzed spectra which should contain terms of the same origin as those of Ph II, namely, Rh I,[6] Co I,[8] and Ni II.[2] All four spectra do, in fact, include equivalent terms, although the two arc spectra are complicated by the additional presence of the structures built on seven *d*-electrons. The $^2D(d^9)$ of Co I has not been found but its position can be estimated at about 30,000 on the scale used in the analysis just referred to. Although the term intervals in Pd II are generally very large, the over-all separations between the lowest and highest levels of the groups of terms are smaller than in Ni II. For example, the 5*s*-group of levels occupies about 5000 wave-numbers less in Pd II than in Ni II. It is particularly noteworthy that $5s^4P$ and bp^4P occupy such relatively low positions.

The author thanks Dr. Meggers, of the Bureau of Standards, and Mr. H. E. White, of Cornell University, for allowing him the full use of their material. Mr. H. A. Blair, of this University, has materially aided the author throughout the investigation.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.
April 5, 1928.

[8] M. A. Catalan and K. Bechert, Zeits. f. Physik **32**, 336 (1925).

METALLIC REFLECTION FROM ROCK-SALT AND SYLVITE IN THE FAR ULTRA-VIOLET

By A. H. Pfund

Abstract

From the rapid rise of the dispersion curve of rock-salt and sylvite in the ultra-violet, the existence of regions of anomalous dispersion in the Schumann region have been long anticipated. By using a specially constructed vacuum tube in connection with a vacuum spectrograph the regions of metallic reflection for NaCl and KCl were found. From these results an estimate was made of the wave-lengths of the true resonance frequencies. The values, 1547A for NaCl and 1581A for KCl, are in remarkable agreement with those previously calculated by Herzfeld and Wolf.

THE development of dispersion formulas by Helmholtz, Ketteler, Lorentz, etc., has made it possible to calculate, from the known dispersion curve of a substance, the characteristic frequencies for the "vibrators" which give rise to anomalous dispersion and metallic reflection. The experimental verification of these formulas has been carried out largely by Rubens and his co-workers as a result of their study of the residual rays from quartz, rock-salt, etc., in the infra-red. More recently Herzfeld and Wolf[1] have calculated the "resonance" wave-lengths of anomalous dispersion in the ultra-violet for the halides of the alkali metals. The present work[2] was undertaken for the purpose of putting these predictions to an experimental test. The existence of "resonance frequencies" is indicated by absorption bands. Due, however, to the great width of these absorption bands for other than extremely thin layers, it was deemed more expedient to search for regions of metallic reflection.

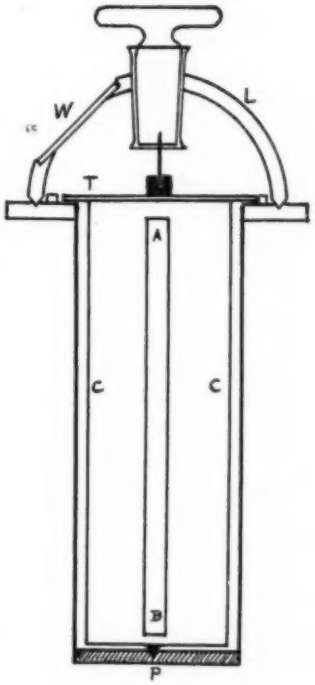

Fig. 1. Film holder.

The vacuum spectrograph was made to accommodate a one-meter concave grating. This was ruled with 15,000 lines per inch and yielded a dispersion of approximately 17.4A per mm. In its original form the spectrograph suffered from the defect that but a single exposure could be recorded on the photographic plate. Fortunately, the opening which received the plate-holder was cylindrical in shape, hence a modified film-holder of the type shown in Fig. 1 could be used to advantage. Since the slit as well as the lines on the grating were

[1] Herzefeld and Wolf, Ann. d. Physik **78,** 35 (1925).

[2] A preliminary notice announcing the discovery of a band of metallic reflection for rock-salt was published in "Science" June 17, 1927.

horizontal, the spectrum was projected in a vertical direction through a vertical slot in the outer cylinder AB. An ordinary kodak film was wrapped around the inner cylinder C and was given the usual coating of mineral oil. This cylinder, which rested on a conical pivot P, could be rotated from without by means of the glass stopper and barrel, which were cemented into the steel dome L. A strip of brass was cemented into a slot cut in the stopper and was made to engage the slotted rod M. So as to be able to observe the rotation of the film-holder for successive exposures a window W was inserted in the steel dome. Then also, coarse graduations were cut on the top T of the film-holder. As a result it was found possible to record at least twenty-five equally spaced exposures on the same film. The departure of the cylindrical surface from the true focal plane of the grating seemed to exert but a negligible effect for present purposes.

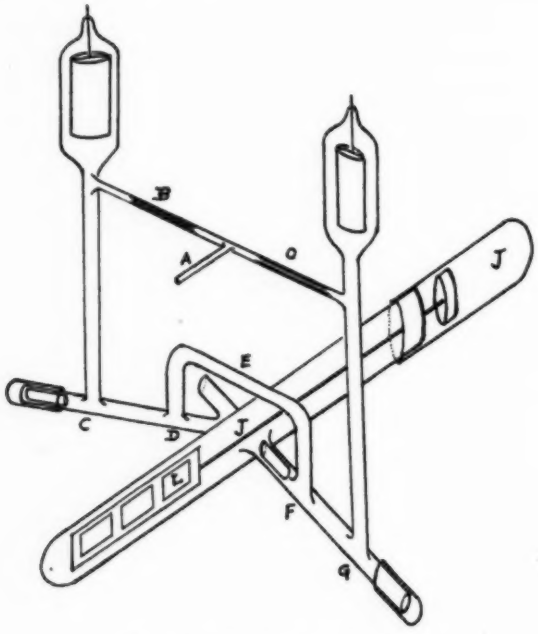

Fig. 2. Diagram of apparatus.

Since it was necessary to record radiations which had been reflected from the surface of the material under investigation and, also, to record "direct" or unreflected radiations, a vacuum tube of special design was employed. As shown in Fig. 2 the gas was admitted through the usual fine capillary into the tube A. So as to prevent the direct passage of the discharge, the tubes connected to A were constricted to a diameter of one half mm, or less at B and O and were wrapped externally with tinfoil. Further, to force the discharge to pass through the arm E and not through the large tube J, the following expedient was adopted: two lengths of glass tubing of about 4 cm each were introduced, respectively, into the arms CD and FG. Each of these short tubes was sealed off at one end and was supplied with a cylinder of

soft iron so as to be susceptible of being moved by means of an external magnet. As shown in the figure, whenever it became necessary to reflect light from the crystal surface, the one tube was moved between *D* and *J*—thus closing this path. The other short tube was moved out of the path of the discharge. Obviously to make use of the direct beam, the relative positions of the two short tubes were interchanged.

The crystals or mirrors to be studied were attached to a metal plate *L* which was constrained to move in "ways." The plate was connected to a thin rod which terminated in a cylinder of soft iron. By means of an external magnet it was possible, therefore, to bring either a mirror or a clear opening in front of the spectrometer slit.

Preliminary spectrograms showed that the entire region from about 3000 to 1000A could be obtained from a mixture of hydrogen and oxygen. Since the electrolysis of water gives rise to a highly explosive mixture, a gas generator was devised which not only eliminated all danger from explosion, but which made it possible to generate hydrogen and oxygen separately or together. The arrangement of parts is shown in Fig. 3. The electrolyte fills the two large outer tubes as well as the central tube *C*, which contains some mercury. A pair of platinum wires *P* less than 1 mm apart is inserted into the tube above the mercury and is connected in parallel with the pair of electrodes *A* (used to generate a mixture of hydrogen and oxygen). As is obvious, the gases generated force the mercury into contact with the free ends of the platinum wires—thus short circuiting the current through *A* and hence, stopping the liberation of gases. Since the electrodes are entirely submerged the danger of an explosion is eliminated. In case the gases are to be generated separately, use is made of the other electrode *B*—the wires at *P* being now connected in parallel with *A* and *B*.

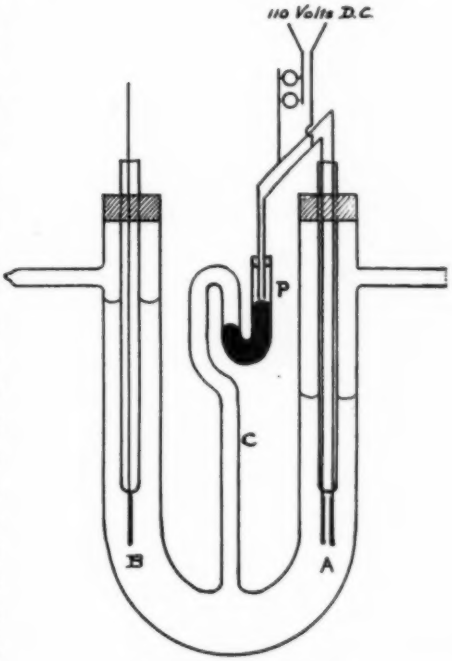

Fig. 3. Gas generator.

The spectrograph was usually exhausted to a pressure of 0.01 mm. At first much time was lost in attempting to obtain reflection spectra from artificially polished surfaces of rock-salt. However, as soon as natural cleavage planes were employed, excellent records were obtained. Not only is the ultimate polish of cleavage planes very high, but the immunity to clouding in consequence of exposure to water vapor is greatly increased. The times of exposure for the "direct" beams was from one to eight minutes

while, for the "reflected" beam the exposure was of the order of one hour. Because of imperfections in the crystal surface, failure to secure perfect alignment, etc., a direct comparison of the intensities of the direct and reflected beams was found not to yield correct results. Since, however, the spectrograms include also the region around 2000A, in which refractive indices and, hence, reflecting powers are known, it was possible to correct for all imperfections and to obtain correct results in the regions of short wave-length.

The actual photographs obtained from cleavage planes of rock-salt (NaCl) and sylvite (KCl) are shown in Fig. 4. It is evident that NaCl has a very pronounced reflection maximum at 1581A, while KCl has a similar

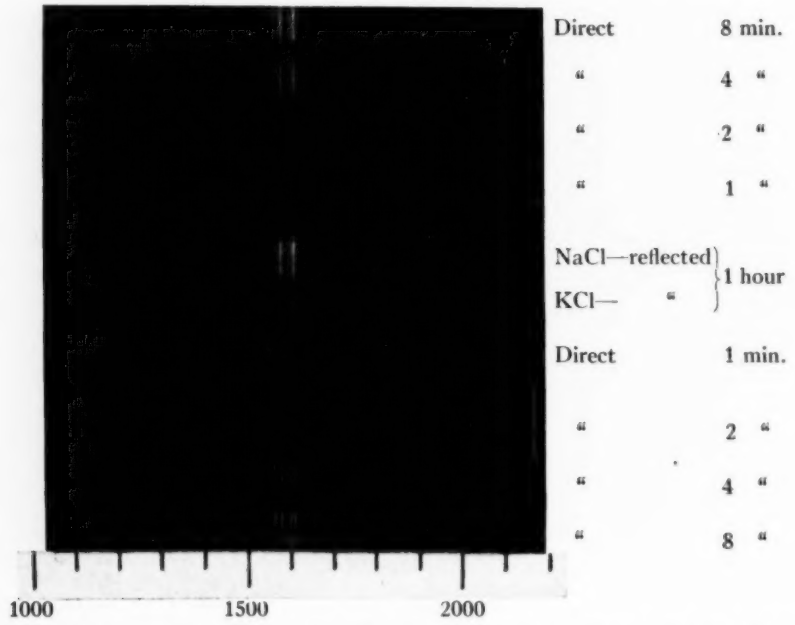

Fig. 4. Photographs of reflection from the cleavage planes of rock salt and sylvite.

maximum at 1616A. Thus the existence of vibrators which occasion the great dispersion of the above substances in the ultra-violet has been established.

As is well known, the region of maximum reflection lies at a wave-length somewhat greater than that of the true center of the absorption band. A tentative estimate of the wave-length of this absorption band was made by taking the wave-length lying midway between the region of maximum reflection and the region on the short wave-length side at which the reflecting power drops, virtually, to zero. According to these estimates the absorption bands are located at 1547A for NaCl and at 1581A for KCl. While not clearly brought out in the reproduction in Fig. 4, it is evident from the finer detail revealed by the negatives that a second maximum in the region of

1100A is being approached. This point is to be cleared up as soon as the work shall have been extended into the region of still shorter wave-lengths.

Among the possible modes of vibration within a crystal, the following may be cited: (1) Vibrations of the nuclei relative to one another. The free periods of these vibrations lie in the far infra-red. Their wave-lengths are 70.2μ for NaCl and 61.7μ for KCl.[3] (2) Nuclear vibrations within a complex positive or negative ion. These vibrations which lie between 6 and 15μ were definitely identified by the writer[4] as originating within the complex negative ion of sulphates and nitrates. (3) Electronic vibrations due to electrons in the outer shells (present work.) (4) Electronic vibrations due to electrons in the inner shells (x-ray region.)

Concerning the vibrations of electrons in the outer shell, it may be stated that Herzfeld and Wolf[1] have predicted the wave-lengths of these resonance frequencies for the halides of the alkali metals. Furthermore, they have been able to identify a given vibrating electron with the positive or negative ion in the crystal lattice. Their results[1] are as follows:

	λ_1 Calc.	λ_2 Calc.	λ_3 Calc.	λ_3' Observed
NaCl	342A (Na ion)	936A (Cl ion)	1543A (Cl ion)	1547 ± 8A
KCl	515A (K ion)	975A (Cl ion)	1580A (Cl ion)	1581 ± 8A

From these data it is evident that the results observed for λ_3' agree within the limits of experimental accuracy with those calculated. Furthermore, the predicted shift of the band for KCl toward the red with respect to that for NaCl, is verified.

In addition to the preceding the following substances were likewise examined: crystalline quartz, glass, calcite, potassium bichromate, zinc sulphide, gold and speculum metal. As for the non-metallic substances, it may be stated that, while none revealed reflection maxima as sharply defined as those of NaCl and KCl, the existence of broad maxima, particularly in the case of calcite, is anticipated. These will require a microphotometer for detailed study. While the reflecting powers of gold and speculum decrease continuously in the region of shorter wave-length, the reflecting power of quartz is on the increase. These results confirm earlier ones[5] which demonstrated the superiority of crystalline quartz over metals in the region of short wave-lengths.

JOHNS HOPKINS UNIVERSITY,
March, 1928.

[3] Fuchs and Wolf, Zeits. f. Physik **46**, 511 (1928).
[4] A. H. Pfund, Astrophys. Jl. **24**, 19 (1906).
[5] A. H. Pfund, J.O.S.A. **12**, 467 (1926).

THE VOLTAGE-CURRENT RELATION IN CENTRAL CATHODE PHOTOELECTRIC CELLS

By Thornton C. Fry and Herbert E. Ives

Abstract

This paper presents a theoretical basis for the interpretation of the experimental results described in the paper which follows. It considers a source of photoelectrons located on the inner of two concentric spheres; derives the trajectory of an electron shot off at any angle with any speed; and then makes use of this information to compute the current which would be received by a small collector located anywhere on the outer sphere upon very general assumptions as to the directional distribution and velocity distribution of the photoelectrons. This theoretical study is followed by graphical presentation of results computed for several typical cases of special interest in connection with the experimental study.

THE work here described was undertaken as a guide to the interpretation of experimental work on the distribution-in-direction of photoelectrons from alkali metal surfaces under varying conditions of illumination. The experimental study, which is described in a paper to follow the present one, was initiated before the field was explored theoretically. Indeed the subject matter of the present paper would probably not have been considered necessary, or have been developed, except for the appearance in the experimental work of a much more complicated state of affairs than a simple qualitative conception of the photoelectric emission phenomena in question would permit. We concluded that it would be helpful, in the interpretation of the experimental results, to have available calculations of what we should expect to get, under different experimental conditions, on the basis of certain simple and plausible assumptions for the distribution-in-speed, and distribution-in-direction of the electrons. Then by comparing the actual results with those predicted we would have a guide to the separation of the real phenomena of distribution-in-direction from the effects of other influences which might distort these. As the sequel will show we were able to effect this separation, and incidentally to show that the distributions in speed and direction which were assumed for purposes of calculation must be substantially correct.

To build up our mathematical theory, we consider a photoelectric cell built of two concentric spheres of radii a and b. (Fig. 1.) At the point E of the inner one is placed an infinitesimal area of photo-sensitive material. The electrons shot out from this differ from one another in two particulars: (a) Their speeds of emissions are not all alike; and (b) They do not all emerge at the same angle to the normal.

If a potential field is established between the two spheres, these electrons are caused to describe curved trajectories and either collide with the outer sphere or return to the inner one.[1] If a collector C of infinitesimal dimensions

[1] It is assumed throughout this discussion that space-charge effects are negligible, which agrees with the experimental conditions.

is located on the outer sphere at the angular distance α from the normal to the photo-sensitive material, this collector will receive those electrons whose trajectories happen to intersect the outer sphere at exactly the right point. How many electrons are received and just which electrons they are will depend upon the angle α and upon the potential difference P between the two spheres, for it is obvious that if the collector is moved to a different position while the voltage is kept constant it will collect those electrons which happen to strike in this new position, the number of which may be either greater or less than was the case in its previous position. Similarly if the voltage is changed without changing the position of the collector the trajectories of the electrons will be altered so that those which would have reached the collector under the old conditions now miss it, while others which would not have reached it under the old conditions now do. The determination of the current to the collector is therefore equivalent to the determination of the number of electrons which leave the cathode with just the proper velocity, and in just the proper direction, to cause their trajectories to intersect the outer sphere at C.

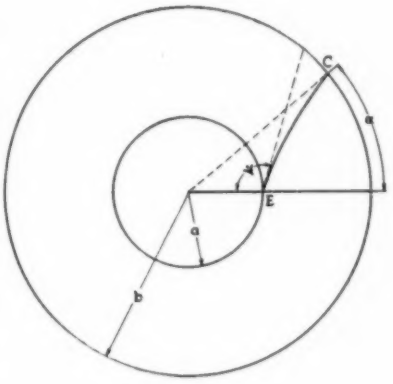

Fig. 1.

Evidently the first thing necessary to a solution of the problem is a knowledge of the trajectory of an electron shot out at an angle ψ to the normal with a velocity v. Since the forces operating between the spheres are central and vary inversely as the square of the distance from their common center, this phase of the problem is identical with the problem of planetary orbits in astronomy. Its solution is therefore well known and need only be copied down. It is

$$r=\frac{v^2a^2\sin^2\psi}{\mu(1-\cos\phi)+v^2a\sin\psi\sin(\phi+\psi)} \tag{1}$$

where r and ϕ are the coordinates of the moving electron, v is the velocity of emission, ψ is the angle of emission, a is the radius of the smaller sphere, b is the radius of the larger sphere, V is the potential difference between the spheres, that is V_a-V_b, and

$$\mu=\frac{-eV/m}{1/b-1/a}.$$

From this point on it is convenient to separate the problem into two parts, considering first the idealized case of a system in which all the emerging electrons have like speeds and differ only in the direction of emission, and then considering separately the general case in which both speeds and direction are variable.

1. *All electrons emitted with like speeds.* The fact that the trajectory of an electron intersects the outer sphere at C serves to determine ψ; for it is only necessary to substitute $\phi=\alpha$ and $r=b$ in (1) in order to obtain an equation in which the only unknown quantity is ψ. In other words, if the velocity of emission v and the angle α are known there is only one angle of emission for which the electron trajectory intersects the outer sphere at C. In order to indicate the dependence of ψ upon the position of the collector, let us call this solution $\psi(\alpha)$.

Now suppose the angular width of the collector to be $d\alpha$, then electrons emitted at angles lying in the range $|d\psi/d\alpha|d\alpha$ will reach the collector, and the total current received by it will be[2]

$$I=-I_0p(\psi)(d\psi/d\alpha)d\alpha \tag{2}$$

provided $p(\psi)$ represents the proportionate part of the electrons which are emitted at the angle ψ, and I_0 is the total photoelectric current.

To determine I, therefore, we need know two things: the function $p(\psi)$ and the function $\psi(\alpha)$. The latter of these is a matter of geometry, and can be determined algebraically from (1). The former is a matter of physical fact, with regard to which the best that can be done in a preliminary test is to make use of Lambert's law,

$$p(\psi)=-2\sin\psi\cos\psi.$$

This gives to (2) the form

$$I=I_0(d\sin^2\psi/d\alpha)d\alpha.$$

As the area of a collector in the form of a zone of width $d\alpha$ extending all the way around the sphere would be $2\pi b^2\sin\alpha\,d\alpha$, and since the electron current would have the same density at all points of such a collector, it follows that the current per unit area would be

$$i=\frac{I_0}{2\pi b^2\sin\alpha}\frac{d\sin^2\psi}{d\alpha}. \tag{3}$$

We have already said that the ψ in this equation represents the result of solving Eq. (1) under the assumption that $r=b$ and $\phi=\alpha$. This solution can be carried out in a perfectly straightforward manner, and an algebraic expression free of derivatives can be obtained for (3). The result is very complicated, however, and of little service from the standpoint of algebraic manipulation, although it can be used for the purpose of making numerical computations in special cases. It is given here for purposes of record only. It is

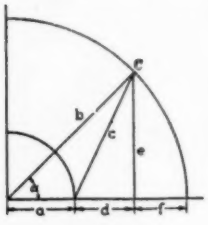

Fig. 2.

$$\sin^2\psi=[ae^2-2\lambda fd+e\,(a^2e^2-4af\lambda d-4\lambda^2f^2)^{1/2}]/2ac^2, \tag{4}$$

where the quantities a, b, c, d, e, f and h stand for the lengths shown in Fig. 2, and where $\lambda=\mu/v^2$. Similarly

[2] Because of the fact that ψ and α are measured in opposite senses, $|d\psi/d\alpha|=-d\psi/d\alpha$.

$$\frac{d\sin^2\psi}{d\alpha}=2\frac{a^2e\sin^4\psi+a[(d-f)\lambda-(d+a)e]\sin^2\psi+\lambda^2 f}{a^2e^2-2d\lambda f-2ac^2\sin^2\psi}. \tag{5}$$

These equations depend essentially upon only one arbitrary parameter λ which is proportional to the potential difference between the spheres and may be written as

$$\lambda=\frac{1}{2}\frac{V}{V_0}\frac{ab}{b-a}$$

where V_0 is the initial energy of the emitted electrons measured in volts. All the other constants which appear in the equation are dimensions of the tube. Therefore the curve obtained by plotting i/I_0 as a function of this variable λ (or, better yet, as a function of V/V_0), may be called a "universal current-voltage curve," meaning thereby that the current-voltage curve appropriate to any initial energy condition can be obtained from it by merely renumbering the horizontal scale. The curves A of Figs. 3 to 10 are of this type and correspond to collectors in the positions $\alpha=10°$, 5°, 15°, 25°, 35°, 45°, 57.5° and 70°, respectively. They are drawn for the ratio $b/a=6$, which was adhered to in the experimental tubes built with concentric spherical electrodes.

It will be observed that as the potential difference between the spheres is increased, the current first rises to a maximum, and then falls off again. Finally so high a voltage is reached that no current flows at all. Geometrically this last condition comes about because of the fact that under such high voltage the radial acceleration is so strong that even those electrons which are emitted tangentially to the cathode reach the anode at a point nearer the axis than the collector. This maximum voltage must obviously be higher the smaller the value of α, a condition which the curves satisfy.

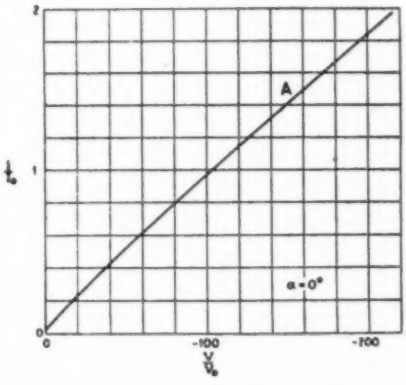

Fig. 3. Voltage-current curve ($\alpha=0°$) computed on assumption that energy of emission is the same for all electrons.

The one anomalous case occurs for $\alpha=0$. Here the current density rises constantly and linearly to higher and higher values as the voltage is increased. This merely reflects the fact that the portion of the outer sphere over which the electrons are distributed becomes more and more restricted as the voltage rises, so that the current density in the neighborhood of the axis increases without limit. It does not follow, of course, that a collector of finite dimensions placed in this position would receive an amount of current which could be made as large as desired by increasing the voltage, for a condition would ultimately be reached in which the entire photoelectric current was flowing to this collector and subsequent increases in voltage would merely restrict

it to a smaller and smaller area of the collector. For this reason the curve for $\alpha = 0$ is of less interest physically than the curves for 5°, and above.

2. *Both speed of emission and angle of emission variable.* If different electrons have different velocities as well as different angles of emission we need

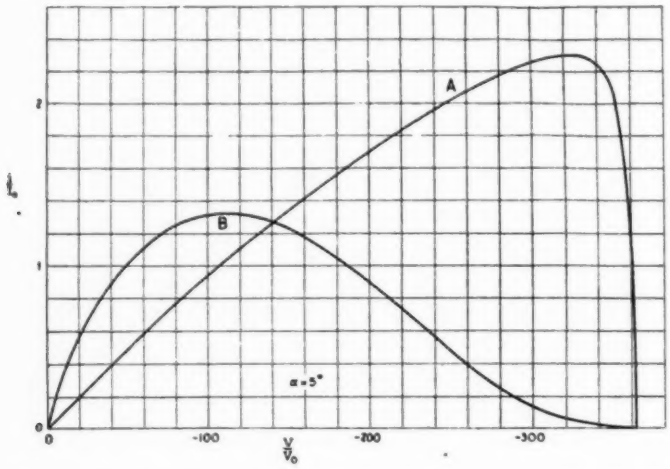

Fig. 4. Voltage-current curves ($\alpha = 5°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula (8).

to know two distribution functions. In the first place, we need to know the proportion of electrons which are emitted at an angle ψ to the normal. This we have already called $p(\psi)$. In the second place, we need to know the way

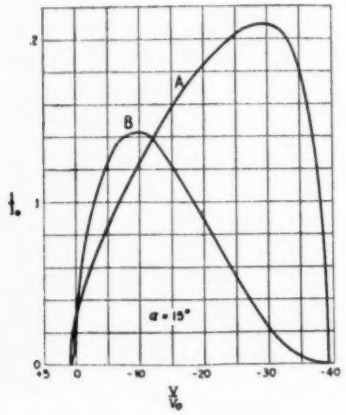

Fig. 5. Voltage-current curves ($\alpha = 15°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula (8).

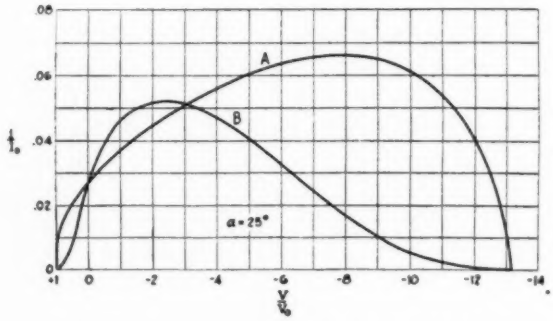

Fig. 6. Voltage-current curves ($\alpha = 25°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula (8).

in which the speeds are distributed among those electrons which emerge at this angle. For this purpose we imagine all the electrons which emerge at an angle ψ to be sorted out and put in a class by themselves, and denote

by $p_\psi(v^2)dv^2$, the proportion of these for which the square of the speed lies between v^2 and v^2+dv^2.

In general, this distribution function will be different for different values of ψ. For instance, it may happen that those electrons which emerge normally

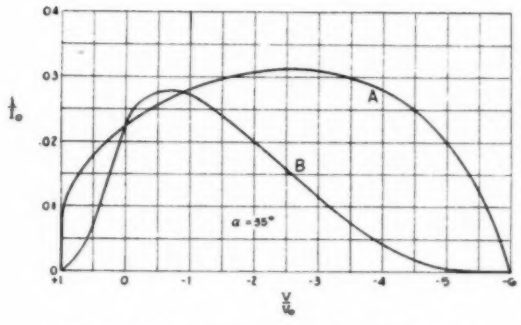

Fig. 7. Voltage-current curves ($\alpha=35°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula (8).

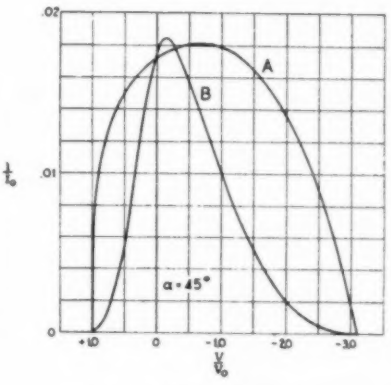

Fig. 8. Voltage-current curves ($\alpha=45°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula(8).

to the surface have on the average a much higher velocity than do those which emerge tangentially, or the converse of this might be true. In the present study we shall *ultimately* assume that this state of affairs does not exist. That is, we shall assume that the proportion of electrons for which the square of the speed is v^2 is the same for the class which emerge at one angle ψ as for any other class. For the time being, however, it is almost as simple to carry through the argument in general as to introduce this simplifying assumption, and it therefore appears advisable to do so in order that the results may be available in case it should become necessary to alter this assumption at some later date.

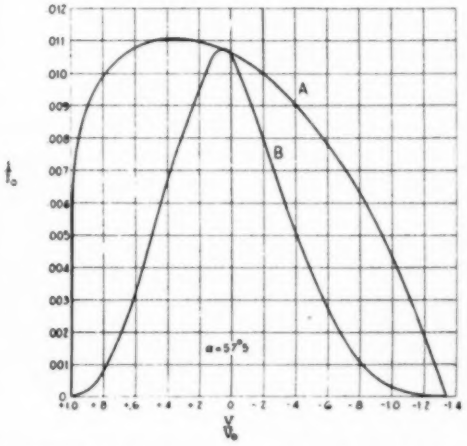

Fig. 9. Voltage-current curves ($\alpha=57.5°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula (8).

An electron leaving the cathode at an angle ψ will reach a collector at *C* if and only if its velocity is related to ψ in such a way that its trajectory intersects the outer sphere at this point. What *velocity* is necessary in order to insure this result may be determined by solving Eq. (1) for v^2, just as in section 1 the *angle* ψ that

was necessary to insure this result was obtained by solving that equation for ψ. Let us denote the square of the correct speed v by the symbol $f(\alpha, \psi)$:

$$v^2 = f(\alpha, \psi).$$

Then the range of velocities which are permissible, if the collector has a finite width $d\alpha$, is $(df/d\alpha)d\alpha$, and the current received by the collector because of electrons which leave at the angle ψ is

$$I_0 p(\psi) p_\psi(v^2) \left| df/d\alpha \right| d\alpha.$$

The total current received by the collector is obtained by integrating this expression with respect to ψ over the entire range of angles which are capable of sending electrons to the collector at all. Formally, therefore, the total current to the collector is

$$I_0 \, d\alpha \int p(\psi) p_\psi(v^2) \left| df/d\alpha \right| d\psi.$$

Since the area of the collector is $2\pi b^2 \sin \alpha \, d\alpha$, the current density is given by[3]

$$i = (I_0/2\pi b^2 \sin \alpha) \int p(\psi) p_\psi(v^2) \left| df/d\alpha \right| d\psi. \tag{6}$$

Aside from the labor of evaluating this integral, the one thing that remains to be done is to determine from the physical conditions of the problem the limits of integration between which it is to extend. That is, it is necessary for us to determine from the physical conditions the maximum

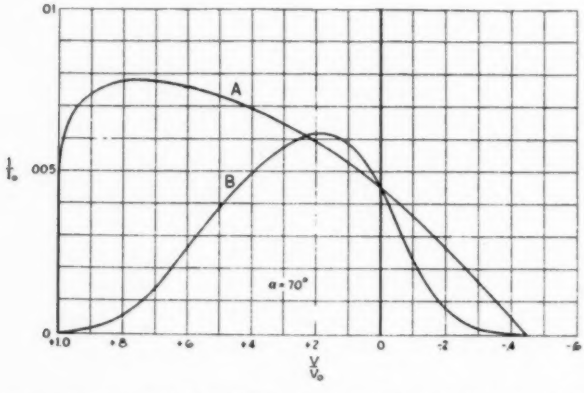

Fig. 10. Voltage-current curves ($\alpha = 70°$). *A*, energy of emission same for all electrons; *B*, energy of electrons distributed in accordance with formula (8).

angle and the minimum angle at which electrons can be emitted, and still reach a collector located at *C*. As the conditions which determine these limits of integration are totally different for the cases of accelerating and

[3] The derivative $df/d\alpha$ is positive for accelerating fields, and negative for retarding fields.

retarding potentials, we shall find it advisable to take up each case separately and treat it independently of the other.

(a) *Accelerating potentials.* Experiments on photoelectric emission justify the belief that there is an upper limit to the velocity of the electrons which are shot out from a target illuminated by light of any specified wavelength. It is not necessarily true that this upper limit of velocity is the same regardless of the angle at which the electron emerges. It may be true instead that the limit is higher for the class of electrons which emerge normally to the surface than for those which emerge tangentially, or vice versa. Be that as it may, however, there is such a maximum value corresponding to each value of ψ, and if we adopt a coordinate system in which the abscissae represent ψ while the ordinates represent v^2, we can plot these limiting values and obtain a curve. This has been done in Fig. 11 in which the curve in question is labeled v_m^2.

This curve must be regarded as experimentally given. It is part of the physical data of our problem and cannot be obtained by any sort of rational argument. Once it is known, however, we are justified in the assertion that no combinations of ψ and v^2 are possible, if, when plotted on the diagram of Fig. 11, they lead to points above the v_m^2 curve.

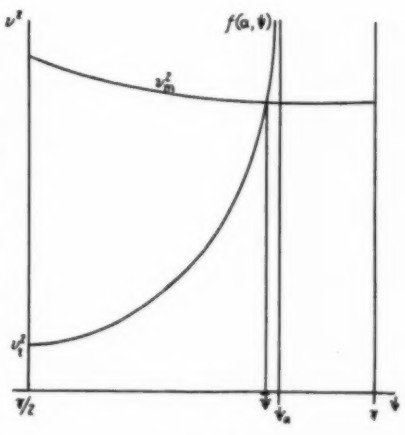

Fig. 11.

On this same diagram we may plot the function $f(\alpha, \psi)$ which gives the square of the speed which an electron, emerging at the angle ψ, must have if its trajectory is to intersect the larger sphere at C. We have already explained how it is to be derived, and it can be accurately plotted if and when we so desire. For the present, however, certain qualitative facts about it are sufficient.

We note, in the first place, that if an electron were to emerge with infinite velocity its trajectory would be straight. Therefore, if it were to collide with the target it would have to be directed at the particular angle ψ_α appropriate to the straight line joining the points E and C. Conversely, if an electron is emitted at this particular angle, it must have an infinite velocity if it is to reach the collector C. It follows that the ordinate to the curve $f(\alpha, \psi)$ must be infinite for the value ψ_α.

In the second place, we note that accelerating fields cause the trajectories to be concave downward.[4] Therefore, if an electron emerges at an angle greater than ψ_α it is bound to miss the collector no matter how great its velocity of emission may be, while if it emerges at an angle less than ψ_α, there is a possibility of it being received by the collector.

[4] That is, toward the axis $\alpha = 0$.

We now turn our attention to those electrons which come off tangentially to the cathode, and note that in general those which leave with the maximum velocity possible to this class reach the outer sphere at a point further from the axis than the collector, while those which emerge with the minimum velocity possible to the class (which is believed from physical considerations to be zero) go straight across and reach the outer sphere near the axis. Somewhere between these two limits is the particular velocity which must be possessed by an elecrron emerging tangentially if it is to be received by the collector. We may denote this by v_t^2. This affords us a second point on our curve for $f(\alpha, \psi)$.

For purposes of argumentation we may draw any curve we please between these two points, such as the one denoted $f(\alpha, \psi)$ in Fig. 11. This curve and the curve v_m^2 intersect somewhere at a value of ψ which we may call $\bar{\psi}$. It is immediately obvious that this is the *largest* angle at which electrons can possibly be emitted if they are to contribute to the current received by the collector C; for otherwise the velocities necessary to insure that their trajectories pass through C [in accordance with the curve $f(\alpha, \psi)$] are greater than the maximum velocities possible at these angles of emission.

On the other hand, from the very geometry of the system, no electrons can emerge at angles less than $\pi/2$. We therefore conclude that the limits of integration which are to be used in this part of our problem are $\pi/2$ and $\bar{\psi}$.

(b) *Retarding potentials.* For retarding potentials the consideration is slightly more complicated. As before we have a maximum velocity of emission for each angle ψ. When plotted this gives us the same curve v_m^2 as before. (See Fig. 12). We also have the same angle of emission ψ_α corresponding to infinite initial velocity, but the trajectories now are concave upward[5] instead of concave downward. It follows that if ψ *is less than* ψ_α, the electrons cannot reach the target at all; just as in the preceding case they could not reach the target if ψ *exceeded* ψ_α. The curve for $f(\alpha, \psi)$, therefore, is now of some such type as that shown in Fig. 12. As before it intersects the curve v_m^2 at a point the abscissa of which may be called $\bar{\psi}$. We conclude that this is the *lower* (not the *upper*) limit of integration.

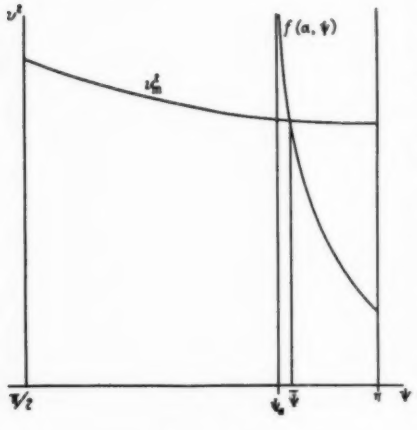

Fig. 12.

At first thought it might appear that the upper limit of integration is π, but this is not the case; for the electrons which are emitted normally to the cathode either travel straight along the axis until they intersect the outer

[5] That is, away from the axis $\alpha = 0$.

sphere, or else they travel along this axis until they are brought to rest by the retarding potential and then retrace their path to the cathode. Similarly, if we consider the class of electrons which are emitted at some such angle as ψ_1, (Fig. 13), we find that those having the highest velocity will travel a path such as EA while those which have very low velocities will travel some such path as EB. The one of these reaches the outer sphere, the other does not. Somewhere between the two there is a limiting velocity which separates those that are capable of reaching the outer sphere from those which are not, and a little consideration shows us that this velocity is the velocity for which the trajectory just grazes the outer sphere.

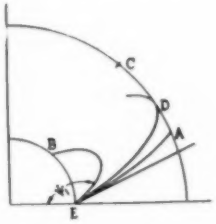

Fig. 13.

If ψ_1 is very nearly equal to π this trajectory will be of the sort represented by ED, and if so, every electron which is shot off at this angle either reaches the outer sphere between the points A and D or else returns to the inner sphere. In no case does it reach the collector C. If we change ψ_1 progressively, both the point D and the point A move away from the axis. Ultimately we reach an emission angle for which D coincides with C. This is the least angle of emission which is capable of placing electrons upon the collector. We designate it by ψ_{min}. As the angle of emission departs still further from π, D and A continue to move away from the axis until an angle of emission is finally reached for which A coincides with C. This angle is the one which we have already called $\bar{\psi}$. If the angle of emission differs from π by more than this amount both A and D lie further from the axis than C and we again reach a condition in which no electrons are capable of reaching the collector at all. Hence we conclude that the limits of integration for the case of retarding potentials are $\bar{\psi}$ and ψ_{min}, the latter being defined as that angle of emission for which the trajectory that just grazes the outer sphere does so at the point C.

This completes the formal part of our argument. It remains only to determine how to compute these limits of integration.

If we assume that v_m^2 has the same value for every value of ψ, the computation of $\bar{\psi}$ is very easy; for it is obvious that $\bar{\psi}$ is simply that angle of emission for which electrons having this velocity reach the collector. This quantity has been evaluated in Section 1, and the solution is furnished us by Eq. (4). As for ψ_{min}, we note that in general there are two values of ψ for which the trajectory intersects the outer sphere at C. For the one of these the electron passes through this point on its way outward from the cathode. For the other it would pass through the outer sphere at some other point if the sphere were merely a mathematical surface through which it could penetrate freely, and after following its trajectory onward would return and intersect the outer sphere again on its way back, this time at C. Both these values of ψ are given by Eq. (4), the one for the positive sign of the radical as written, the other for the negative sign. The condition of grazing incidence

is reached when these two values coincide: which means, of course, when the quantity under the radical sign vanishes. It follows that

$$\sin^2 \psi_{\min} = (ae^2 - 2\lambda fd)/2ac^2,$$

where λ is a root of the equation

$$a^2e^2 - 2af\lambda d - 4\lambda^2 f^2 = 0.$$

3. *Numerical computations.* For the purpose of numerical computation we assume Lambert's law,

$$p(\psi) = -2 \sin \psi \cos \psi, \tag{7}$$

as before, and for the function $p_\psi(v^2)$ we adopt the same parabolic formula as was used in our paper on "The Voltage-current Relation in Central Anode Photoelectric Cells,"[6] namely,

$$p_\psi(v^2) = \frac{6}{v_m{}^2}\left[\frac{v^2}{v_m{}^2} - \frac{v^4}{v_m{}^4}\right], \tag{8}$$

which represents the experimental data very satisfactorily.

The function $f(\alpha, \psi)$ is obtained directly from (1). It is

$$f(\alpha,\psi) = \frac{\mu(\cos\alpha - 1)}{ab \sin\psi \sin(\alpha+\psi) - a^2 \sin^2\psi} \tag{9}$$

from which it is found that

$$\frac{\partial f}{\partial \alpha} = \frac{-v^2}{\cos\alpha - 1}\left[\sin\alpha + \frac{ab}{\mu} v^2 \sin\psi \cos(\alpha+\psi)\right]. \tag{10}$$

When (7), (8), (9) and (10) are substitued in (6), and this equation is integrated between the limits above given, definite numerical results are obtained from which current-voltage curves may be plotted. It turns out again that the only essential parameter in the computation is $\mu/v_m{}^2$, which we may write as

$$\lambda m = \frac{\mu}{v_m{}^2} = \frac{1}{2}\,\frac{V}{V_0}\,\frac{ab}{b-a},$$

where V_0 is the maximum energy of emission, measured in volts. Hence these curves may be plotted once for all, regardless of the maximum velocity of emission. In other words, the curves for different wave-lengths of light should be identical, except for a constant scale factor, so long as the dimensions of the cell and other physical conditions remain unchanged.

Such curves have been computed for angles[7] 5°, 15°, 25°, 35°, 45°,

[6] H. E. Ives and T. C. Fry, Astrophysical Journal, LVI, No. 1, July, 1922.

[7] The case of $\alpha = 0°$ is omitted; for while our method of computation gives the *current density* correctly at this angle, the current to a small collector cannot legitimately be found by multiplying this current density and the area, for the reason explained at the close of §1. Moreover, it is no longer true, as in §1, that the result thus obtained is correct so long as it does not exceed the total available current; for the low-velocity classes are completely absorbed by the plate at lower voltages than are the high-velocity classes, and immediately begin to give excessively high *densities* at the center of the collector.

57.5° and 70° respectively, and are shown in the curves *B* of Figs. 4, 5, 6, 7, 8, 9, 10. The value of b/a is again 6. They are shown plotted together in Fig. 14, each multiplied by the factor sin α. They therefore correspond to currents received by the complete horizontal zones corresponding to their

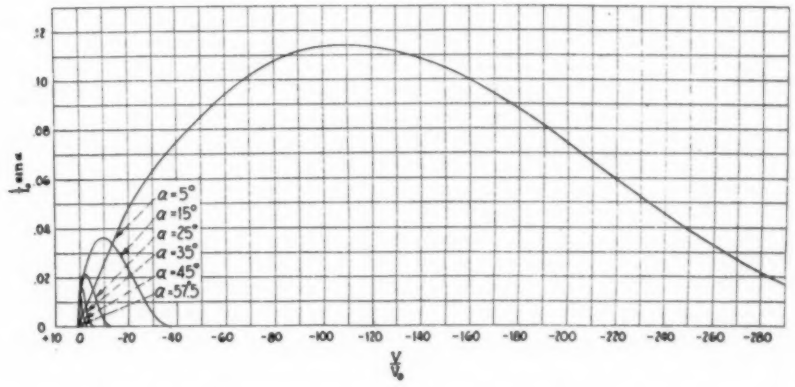

Fig. 14. Showing total current to zones at various angles α from the normal to illuminated cathode.

respective angles rather than to currents per unit area. The summation of such curves as those shown in Fig. 14 for all possible angles should of course be (except for a constant factor) the voltage-current curve obtained by using the entire anode.

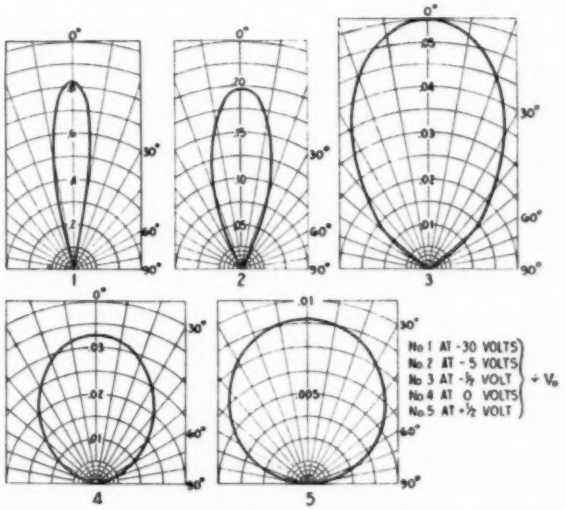

Fig. 15. Angular distribution of electrons for various cathode voltages.

Examination of these curves shows them to possess very characteristic shapes. Comparison of the experimental curves with these should give an excellent check on the correctness of the assumptions underlying the theory. Attention may be called particularly to the shift of the maximum of emission

in Figs. 4–10 from accelerating to retarding potentials as the angle of the collector with the normal increases.

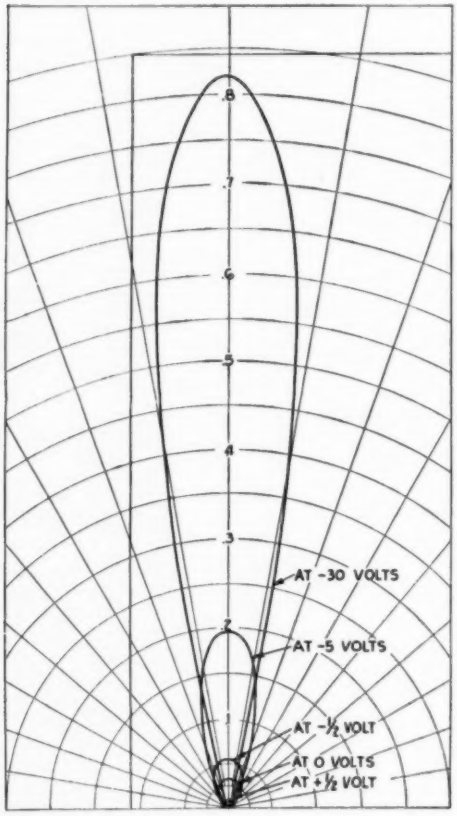

Fig. 16. Showing relative magnitudes of angular distribution curves of Fig. 15, for various cathode potentials.

In Fig. 15, (1), (2), (3), (4), (5) and in Fig. 16 the same results are plotted in polar coordinates for values of V/V_0 of $+1/2$, 0, $-1/2$, -5, and -30. These curves show the results which are to be expected when, for instance, an exploring finger of fixed area is rotated about the point of electron emission. A very important point shown by these curves is that the true initial direction distribution is manifested, not at zero applied field, but with a certain retarding field. Thus the curve for zero field, Fig. 15 (2), is a decided ellipse with its long axis normal to the surface, while the curve for $+V/2V_0$ (*cathode voltage*) is very nearly a circle (that is, the distribution assumed). This behavior is of course due to the fact that the point E, Fig. 1, is not at the center of the collector; so that even those electrons which leave E tangentially to the cathode reach the anode at $\alpha = 80°$, instead of $\alpha = 90°$. Only with the emitter at the exact center of the sphere would the true distribution be obtained.

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THE DISTRIBUTION IN DIRECTION OF PHOTOELECTRONS FROM ALKALI METAL SURFACES

By Herbert E. Ives, A. R. Olpin and A. L. Johnsrud

Abstract

An experimental study of the distribution in direction of photoelectrons emitted from alkali metal surfaces irradiated by light incident at varions angles and polarized in different planes.—The alkali metal surfaces used were of two sorts: (1) liquid alloys of sodium and potassium, (2) thin films of potassium or rubidium on polished platinum. In all cases the alkali metal surface was at the center of a large spherical enclosing anode, provided either with collecting tabs at various angular positions or with an exploring finger. It is found that the emission closely obeys Lambert's law, but that the ellipse by which the emission is represented, in polar coordinates, is more elongated normally to the surface for perpendicularly incident light than for obliquely, when the direction of the electric vector is in both cases parallel to the surface, and still more elongated for obliquely incident light with the electric vector in the plane of incidence. The distribution curves are all perfectly symmetrical about the normal to the surface, showing no tendency to follow the direction of the electric vector.

Introduction

THIS investigation was undertaken for the purpose of acquiring additional information on the striking differences in photoelectric emission from certain alkali metal surfaces when the plane of polarization of obliquely incident light is changed. The well-known variations in emission as the electric vector is altered from vibrating parallel to the plane of incidence to vibrating perpendicular to it are two in number; first, a change in the amount of the emission, much greater in the characteristic cases than can be accounted for by the gross optical absorption of the surface; and second, the development of a pronounced maximum in the spectral distribution of emission. In addition to these well extablished effects, work by Hughes[1] some ten years ago indicated a difference in the direction of emission of photoelectrons as the plane of polarization of the exciting light was changed. It was for the purpose of obtaining more exact information on this point than Hughes' work afforded that this investigation was made. Our data, as will be seen, confirm Hughes' conclusions, but are more detailed and complete in a quantitative way than his.

Direction distribution measurements of photoelectrons from other than alkali metal surfaces have been made by Gardner,[2] who used a platinum surface and measured the photoelectrons received by an exploring finger in various angular positions with respect to the emitting surface. He found the emission to be greatest normal to the surface, falllng off rapidly therefrom. His work will be discussed further in the consideration of our own.

[1] Hughes, Phys. Rev. **10**, 5 (1917).
[2] Gardner, Phys. Rev. **8**, 70 (1916).

The distribution-in-direction of photo-electrons produced by x-rays has been the subject of considerable study recently; particularly by the cloud expansion method.[3] The results of these experiments are generally in agreement with the idea that the photoelectrons tend to follow the direction of the electric vector. Since there have been various suggestions that the peculiar behavior of the photoelectric emission from alkali metal surfaces may be due to a similar tendency for the electrons to follow the electric vector, it is a matter of some interest to determine if such is the case. The work of Hughes, above quoted, was not done with apparatus which would make possible an unambiguous answer to this question.

Terminology

Pohl and Pringsheim[4] in their extensive and important work on the photoelectric effect assumed that the great enhancement of the photoelectric emission when the electric vector is parallel to the plane of incidence is always associated with the presence of a maximum of emission in the spectrum, characteristic of the material (although the converse of this was not always true.) They also assumed that these two effects were both characteristic of the pure alkali metals, for instance sodium and potassium, although their actual work, in which the two effects were present together, was done on sodium-potassium alloys. The photoelectric emission due to light polarized with the electric vector perpendicular to the plane of incidence was called by Pohl and Pringsheim the "normal" photoelectric effect, that due to light polarized with the electric vector parallel to the plane of incidence they called the "selective" photoelectric effect. These terms have come into very general use.

Recent work has shown that the assumptions as to the invariable association of enhanced emission with a spectral maximum characteristic of the material, and of these properties being characteristic of the pure alkali metals, cannot be supported.[5] The pure alkali metals, while showing a spectral maximum, do not exhibit the large ratio of emissions. Their alloys exhibit varying ratios of emission depending on their exact composition.[6] Again while the pure alkali metals, in the liquid state, do not exhibit the large ratio of emissions, they exhibit this phenomenon to a remarkable degree, when present in the form of thin films upon other metals such as platinum. A thin film of alkali metal does not however exhibit a spectral maximum, at the wave-length formerly supposed to be characteristic of it.[7]

It is evident from these facts that the terms "normal" and "selective" are inadequate to describe all the observed phenomenon with proper discrimination and that to group together, under these terms, all the

[3] See Watson, Proc. Nat. Acad. Sci. **13**, No. 8 (1927) for references.
[4] See Pohl and Pringsheim, "Die Lichtelektrische Erscheinungen," Viehweg, 1914.
[5] Ives and Johnsrud, Astrophys. J. **60**, 4 (Nov. 1924).
[6] Ives and Stillwell, Phys. Rev. **29**, 252 (Feb. 1927).
[7] Ives, Astrophys. J. **60**, 4 (Nov. 1924).

phenomena of emission which occur as the plane of polarization is changed would be dangerous.

In addition to the reasons given for not using the terms "normal" and "selective," we have an additional fact which has come out of the present work. It has been commonly assumed that the "normal" effect is obtained either with obliquely incident light in which the electric vector is parallel to the surface, or with perpendicularly incident light, since the electric vector is in this case also parallel to the surface. We have, however, in this work, found differences in the distribution curves for those two cases, that is, differences which depend solely upon the angle of incidence. We have then, if possible, to find terms to describe the three following cases: First, normally incident light, in which the electric vector is of necessity parallel to the surface. Second, obliquely incident light in which the electric vector is perpendicular to the plane of incidence. Third, obliquely incident light in which the electric vector is parallel to the plane of incidence. The choice of appropriate terms has proved a matter of great difficulty. The choice is complicated by the fact that the definition of "plane of polarization" which is used in physical optics was unfortunately chosen so that it conveys just the opposite idea to that which we wish when considering the direction of vibration. It would make the present paper excessively long, and would make the descriptions of experimental additions exceedingly clumsy, if phrases or adjectives completely descriptive of the conditions of incident llght were used in every case. It has therefore been decided to make this description by means of symbols. In order to make our descriptions conform as closely as possible to previous work, we have used the symbols introduced by Pohl and Pringsheim for obliquely incident light polarized in the two characteristic planes, and have added to these a third symbol for normally incident light. In accordance with this decision the symbols with their meanings are as follows: $\doteq$–normally incident light (electric vector parallel to the surface); $\parallel$–obliquely incident light, with the electric vector parallel to the plane of incidence; $\perp$–obliquely incident light with the electric vector perpendicular to the plane of incidence.

Apparatus

The photoelectric cells used for this study were of special design approximating more or less closely to the simple geometrical form considered in the theoretical study reported in the preceding paper.[8] In all cases the cathode was at the center of a spherical enclosure which formed the anode. Several forms of cathode were used in various cells. In the earliest work, a flat polished platinum plate was used on which a sensitive alkali metal surface was formed by sublimation, as described in earlier papers. In later cells the cathode was a hollow spherical platinum ball of dimensions such that the complete cell approximated very closely to the form postulated in the theoretical study. The photoelectric surface was formed in these cells by

[8] Fry and Ives, Phys. Rev. **31**, 000 (1928).

sublimation. In other cells the cathode was of liquid sodium-potassium alloy in a cup. To insure against charging of the walls of this cup the glass

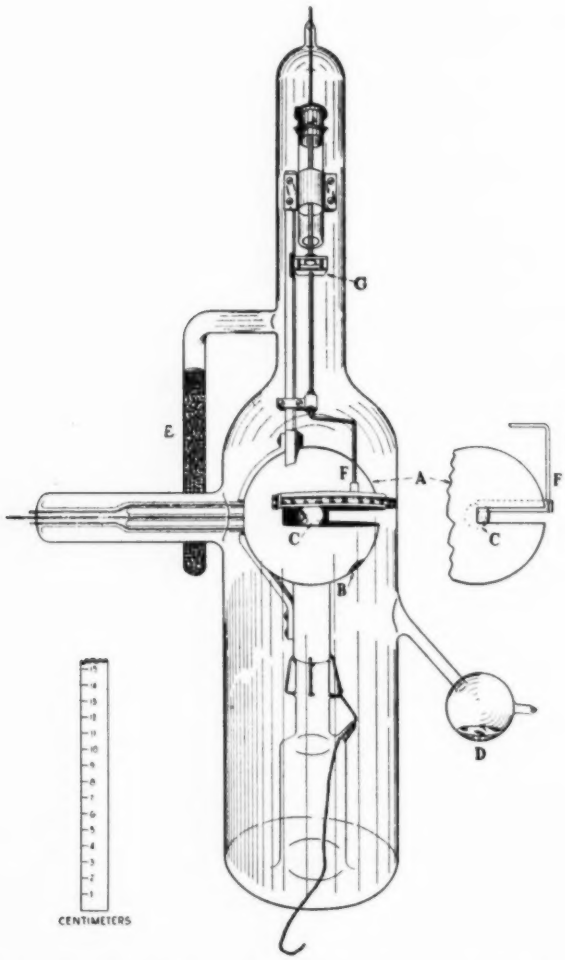

Fig. 1. Moving vane type of photoelectric cell. The anode *A* consists of a spherical copper shell, coated inside and out with turpentine soot. Concentric within is the hollow spherical platinum ball *C* used as cathode. Rb was sublimed from side tube *D* through opening *B* of anode onto the cathode. The thickness of cathode layer could be controlled by heating the filament within the Pt ball. Light focussed on the cathode was incident and reflected through a narrow slit in side of anode. Electrons reaching anode at any angle with respect to normal to cathode could be measured by setting the moving finger *F* at that angle, the angular setting being made by rotating iron coupling *G* with electromagnets. In order to insure that the position of the finger in no way influenced the field between cathode and anode, a curved strip of soot-coated copper was fastened to the anode directly behind the path of the movable finger as shown in inset. Charcoal tube *E* was immersed in liquid air to insure a good vacuum.

was nickel coated and the alloy flowed in until flush with the top. Details of two representative designs are shown in Figs. 1 and 2. During the course

of the study, measurements were made on eleven different photoelectric cells conforming more or less closely to the types shown.

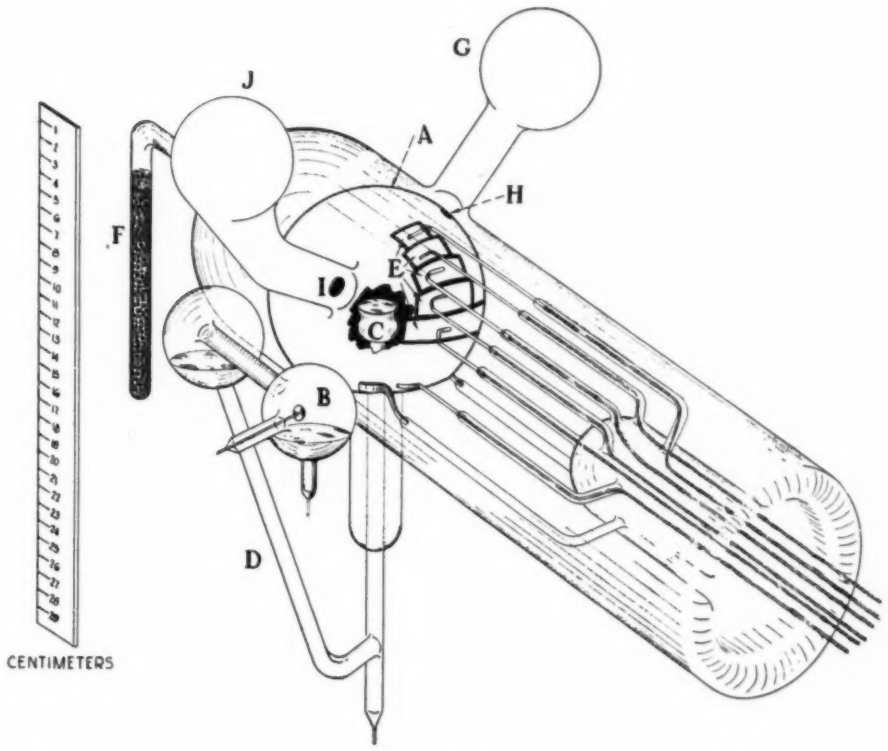

Fig. 2. Isolated tab type photoelectric cell. Soot-coated copper shell *A* serves as anode and nickel-plated glass cup *C* filled with NaK alloy forms the cathode. After evacuating cell the alloy was poured from side tube *B* (which has electrodes for measuring the ratio of photoelectric emissions for light ∥ and light ⊥) through connecting tube *D* and allowed to rise in cup *C* until the level was exactly that of top of cup. Light was incident by way of side tube *G* through small hole *H* onto alloy surface and reflected through opening *I* into side tube *J* where reflected around and around until absorbed entirely. Tubes *G* and *J* were blackened completely with exception of nose of *G* wherein the light entered. Isolated tabs *E* having separate lead-in wires collected the electrons at various angles with respect to normal to cathode. Charcoal tube *F* placed in liquid air maintains good vacuum.

For purposes of reference the following list shows the structural type of each of the cells for which experimental data are given in the figures illustrating the paper.

Cell No.		
	70 K	Moving vane, flat platinum plate cathode.
	119 Rb	Moving vane, spherical platinum cathode.
	121 Rb	Flat platinum plate cathode, entirely enclosing anode without tabs or vane.
	165 Na K	Multiple tab, liquid alloy in cup.
	171 Na K	" " " " " "
	183 Na K	" " " " " "
	187 K	Multiple tab, solidified potassium in cup.

In order to make the necessary measurements for different angular positions from the cathode, two different devices were used. In certain of the cells a moving finger was provided arranged to rotate between a double wall in the anode, thus providing for an unchanging electrical field while at the same time the current to be measured was only that received by the small area. This form of cell is shown in Fig. 1. In other cells a number of isolated tabs were placed at appropriate positions in the spherical anode and were connected to separate leading-in wires. Such a cell is shown in Fig. 2 and the general method of electrical connection is shown in Fig. 3.

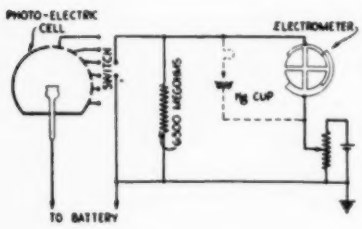

Fig. 3. General method of electrical connection. (See Fig. 4 also.)

In all the work here described except where otherwise noted, the exciting light was blue light of wave-length 4358 of the mercury spectrum as obtained from a quartz mercury arc and filtered through a special filter of blue glass combined with several layers of aesculin in gelatin. This filter while transmitting the blue light, eliminated the violet line at 4038 so completely that extreme over-exposure in a quartz spectrograph failed to show any trace of it.

In the greater part of the work the obliquely incident light was incident at an angle of 60° and was passed through a multiple Ahrens prism for polarization purposes. The prism was arranged so that its azimuth could be changed by cords operated by the observer.

All measurements were made with a Compton electrometer, the steady deflection method being used, that is, the electrometer measured the potential drop across a high resistance in series with the cell. As a high resistance, a xylol-alcohol sealed cell with a resistance of 6,500 megohms was used. Thus with 90 volts on the needle a sensitivity of approximately 300 cm/volt was obtained. The electrometer was enclosed in an air-tight box with drying material and the photoelectric cells were similarly entirely enclosed. Fig. 4 shows a photograph of the photoelectric cell box open with a cell in place. In the foreground will be seen a series of six cords operating mercury switches. These were used with those of the cells in which the receiving tabs were fixed in position and provided means for switching from one electrode to another. In this respect the tab cells were better than the finger cells, for with these it was necessary to open the door of the iron box encasing the photoelectric cell every time adjustment for a new angle was made. Thus the finger cells were usable only on dry days. As a matter of fact, the finger cells were used only when the other type was inadequate.

Details of Measurements

A series of measurements for showing the distribution of photoelectrons in direction for any condition of the exciting light consists of successive measurements either with a measuring finger in a series of positions or from

several of the isolated tabs in the spherical anode. The comparatively simple procedure just outlined is, however, greatly complicated by experimental difficulties. One of the most serious difficulties of all in the present study has

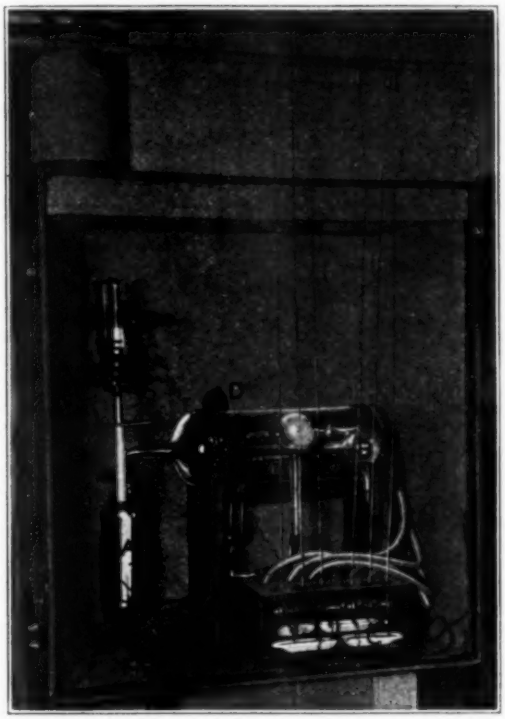

Fig. 4. Photograph of a photoelectric cell in place. *A*, liquid air flask on charcoal tube; *B*, small photoelectric cell connected with large one to permit study of relative emissions for light ∥ and ⊥ before pouring alloy into cathode stem of large cell (Fig. 2); *C*, switching device whereby each tab of cell (Fig. 2) can be disconnected from ground and connected to the electrometer in turn by pulling proper silken thread leading out through top of shielding box; *D*, lens and prism unit through which light was admitted; *E*, xylol-alcohol resistance across electrometer; *F*, carefully insulated and shielded wire leading to electrometer.

been the characteristic one in working with alkali metals in high vacua that all parts of the apparatus become photo-sensitive. The nature of the errors due to this cause are strikingly illustrated by Figs. 5 and 6. In these figures the crosses represent the distribution curve as obtained by a finger moving in the plane of incidence, with obliquely incident light. The distribution is represented by an ellipse. The small circles show the results obtained with light incident normally on the surface. In this case the distribution curve consists of two wings separated by a pronounced depression in the middle.

This apparent difference between the distribution curves for the two illuminations is entirely spurious, and is due to the fact that the flat platinum plate which was the cathode reflects light directly back to the exploring finger when it stands opposite the plate. The result is a photoelectric current back

from the finger which may be so great as actually to carry the minimum to negative values, as shown in Fig. 6. This sensitiveness of the collector is also exhibited when voltage-current curves are made to the entire collector by a current in the reverse direction when the central electrode is made positive.

In order to prevent the anode from becoming sensitive, we have made use of an earlier observation that carbon, in particular soot, does not absorb alkali metal vapor to the point of becoming sensitive to light nearly so quickly as most of the metals do. The spherical anodes were accordingly in all cases given a coating of soot. Even so, in the course of time some sensitiveness develops, particularly for long wave radiation, so that it was necessary to make frequent voltage-current curves to make sure that no sensitiveness had developed. Because of the fact that the sensitiveness developed by the soot coating was relatively greater for long wave energy than the sensitive-

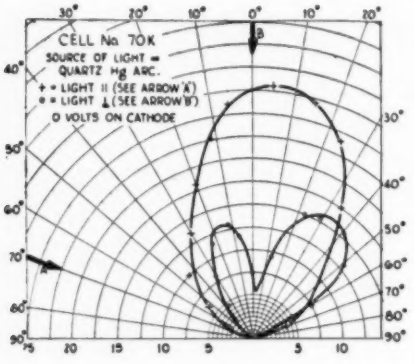

FIG. 5

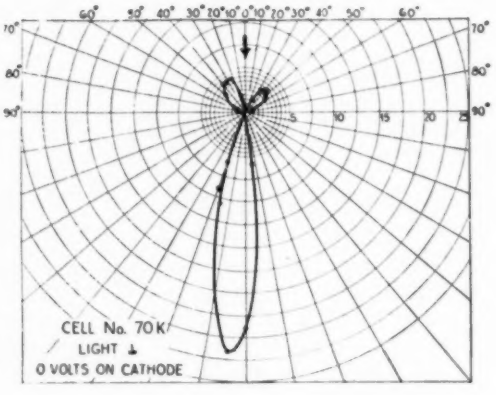

FIG. 6

Fig. 5. Distorted angular distribution curve. Counter-emission of electrons from a photo-sensitive anode greatly decreased the measured current for settings of finger such that light was reflected on it. Arrows show direction of incidence of light.

Fig. 6. Showing still greater distortion of angular distribution curve. For settings of finger at small angles to normal and light normally incident, anode to cathode current was much larger than that from cathode to anode.

ness of the cathode, it was not possible to make satisfactory distribution curves with green or yellow light.

The danger of back currents from the anode when photo-sensitive makes careful and accurate optical alignment extremely important. Accuracy in these adjustments is essential for other reasons. If, for instance, the lens and prism set-up should be such that the path of the incident light were at any place deviated from a straight line the effect of rotating the prism would be to shift the position of the incident beam on the cathode. The result would be that the angle between the normal at the illuminated spot and a fixed collector might vary slightly for light $\perp$ and light $\parallel$, the apparent photo-electric sensitivity of the spot illuminated might vary with the polarization of the light, and, of greater importance still, the reflected light might fall more directly on the anode in one case than in another. This latter problem

was a serious one in that the incident light beam had to be introduced onto the cathode through a small opening in the spherical metal anode and the reflected beam allowed to pass out of the tube through a similar opening.

To facilitate the problem of getting the light onto the cathode and out of the cell again without illuminating the anode in any way the beam was made as small as possible. This small beam was obtained by passing the light from the arc through a specially constructed collimator having within it soot coated apertures of about 6 mm diameter at intervals of 2 to 4 cm. This cut out all the effects that might result from stray or reflected light. The direct beam then passed through a carefully machine-centered lens and prism system; one lens changing the light to parallel rays while it passed through the multi-Ahrens prism and the other focussing the polarized light on the cathode of the photoelectric cell. An additional diaphragm or aperture reduced the width of the pencil still more before it entered the cell.

Fig. 2 shows an added precaution taken in the case of some of the more important cells. On the side of the incident light and projecting toward the source was an arm of the tube blackened on its sides. Any diffused light that may have originated as the incident beam passed through the glass wall at the end of this arm was absorbed by the black walls of this tube. Then, after the light was reflected from the cathode through the small opening in the anode, it entered another arm blackened on the outside and shaped to form a light trap.

While this cutting down to a minimum of the size of the incident light pencil inevitably reduced to some extent the accuracy of the results, this condition was necessary to permit reliable comparison of the observed deflections for light polarized in different planes and for different angles. By keeping the electrometer deflections small the *IR* drop across the high resistance was made negligible and the tab or finger was kept at the same potential as the remainder of the anode. Moreover, the more nearly the illuminated spot assumed infinitesimal proportions the more nearly the observations should approach the theoretical requirements, particularly where the cathode consisted of a small sphere.

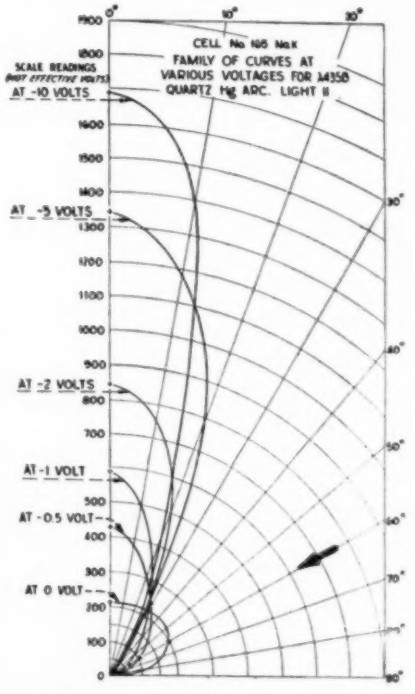

Fig. 7. Angular distribution of electron emission for various accelerating potentials. Arrow shows angle of incidence of light.

In order that the size of the currents might not fall to inconveniently low values for the tabs at large angles to normal from the cathode, these tabs

were in several cells increased in dimensions for the larger angles as shown in Fig. 2. The results then obtained were reduced to the current per unit area basis for study. This gradual increase in the size of the tabs with α would not have been permissible had not the moving vane type photoelectric cell first revealed the symmetry of the angular distribution curve about the normal to the surface.

Early in the work we had to consider the question of the proper value for the applied electric field. It was found that the distribution curves varied from a flat to a long ellipse as the potential difference between cathode and anode was increased. This phenomenon is of course entirely to be expected since the stronger the accelerating field the greater the proportion of the electrons ejected at large angles of incidence which will be deviated toward the normal. This effect is discussed in the theoretical paper already referred to and is illustrated by the experimental data of Fig. 7. The curves connecting the limited number of experimentally determined points were drawn according to the theory worked out by Fry and Ives.

The first assumption would probably be that the field to use would be the effective zero, which is to be determined by taking a voltage-current curve to the complete anode and finding the point at which saturation occurs. Actually, as has been pointed out in the theoretical study, the true initial distribution-in-direction occurs at zero field only if the emitting element is at the exact center of the spherical anode. Where, as is the case with the concentric spherical electrodes, chosen, for reasons of simplicity, in calculating the effects of various applied fields, the emitting element is off center, the true initial distribution is represented most nearly at some small retarding potential. The experimental results are hence subject to interpretation by reference to the design of the tube used.

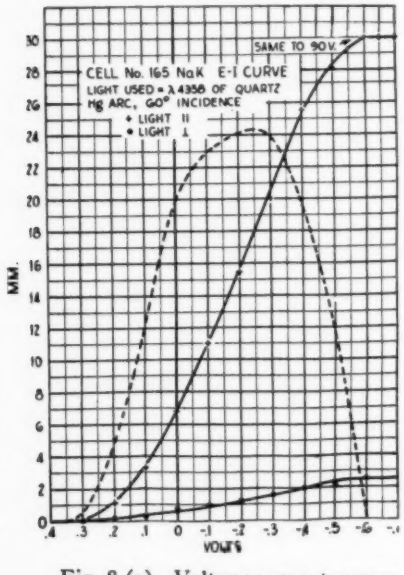

Fig. 8 (a). Voltage-current curves taken soon after cell was made. Broken line shows relative energy distribution of emitted electrons as given by derivative of *E-I* curve.

Experimental Results

As a starting point for a study of the direction distribution curves, it is necessary to determine the voltage-current curve for the total current received by the enclosing anode. As already noted this gives the effective zero, as conditioned by contact potential differences, which may vary from time to time with the amount of absorption of the alkali metal by the soot covered anode. Fig. 8 (a) shows a pair of voltage-current curves for monochromatic light of wave-length 4358 taken with $\perp$ and $\parallel$ light. Fig. 8 (b) shows a similar pair taken three weeks

later after the soot coating had absorbed enough alkali metal to shift the saturation point, but not enough to produce a current in the reverse direction for + voltages. These are representative of the kind of curves taken frequently during the course of the investigation to determine the effective zero. A point of considerable importance is immediately evident on inspection of Fig. 8 (b) where the curves are plotted as percentage of saturation current value. *This is that the curves for ⊥ and ∥ light are identical in shape.* The maximum energy of emission of photoelectrons is the same for both and the distribution of initial energies is the same. This is in agreement with the recently published work of Wolf.[9] The dashed curves are the derivatives, showing the numbers of electrons emitted at various initial energies. While the curves shown were obtained from deep pools of alloy, exactly similar curves are obtained from the thin film cells, in which the layer of alkali metal is only a few atoms thick at most. These curves closely approximate to the parabolic law assumed in the previous theoretical study. The

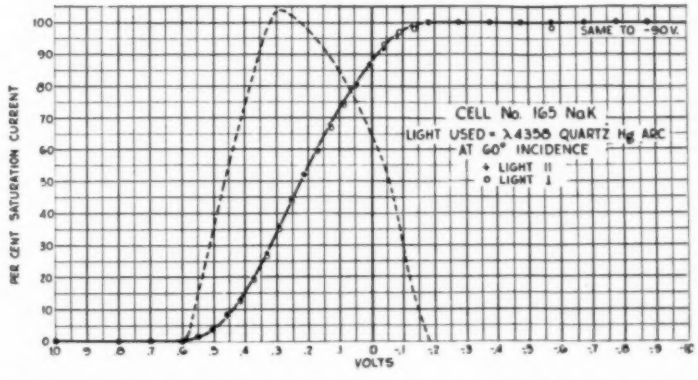

Fig. 8 (b). Voltage-current curves taken a few weeks after cell was made. Compare Fig. 8 (a).

distribution according to velocity is clearly not the Maxwell distribution frequently assumed in theoretical discussions.

The conclusion that the voltage-current curves are alike for ∥ and ⊥ light, is subject to qualification under certain experimental conditions. It has been a matter of frequent observation in our work that it is difficult to secure good saturation when using exciting light of long wave-length, i.e., near the photoelectric threshold. It has further been found that when this difficulty of attaining saturation is encountered, it is greater with ⊥ than with ∥ light. As the result of many experiments we have found that the occurrence of good saturation conditions for long wave excitation is definitely correlated with the completeness of the evacuation of the cells. In the type of cells here described, with their large soot coated surfaces, the necessary vacuum for complete saturation at zero fields is often attainable only by the use of liquid air on the attached charcoal tube; even so it is usually difficult to attain this condition for excitation by light near the photoelectric threshold, that is,

[9] Wolf, Ann. d. Physik **83**, 7 (1927).

for slow electrons. The behavior of a typical cell when excited by lights of various colors, is shown in Fig. 9. With blue light complete saturation is attained at zero field when the gas pressure is held to its minimum value by the use of liquid air on the charcoal tube. Without liquid air the discharge

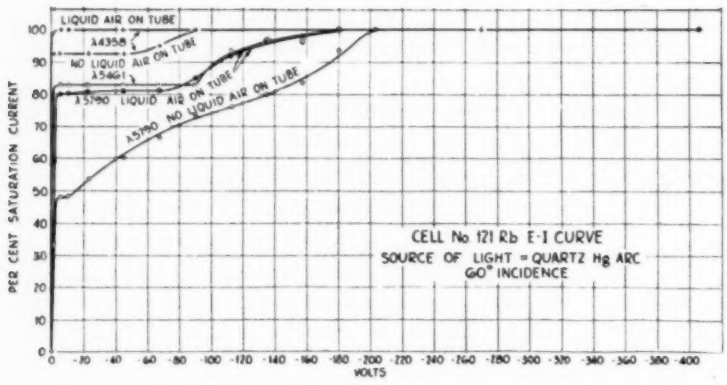

Fig. 9. Comparison of voltage-current curves for imperfect vacuum central cathode cell under illumination with monochromatic light of various wave-lengths. Note better saturation at low voltages with improved vacuum.

attains apparent saturation at zero field, but, at considerably higher voltages (50–60) the current again increases, slowly, to a new saturation value approximately 10 percent higher, which is unaffected by further increase of the field (at least up to 400 volts). The same type of behavior is shown under excitation by green and yellow light, except that the difference between the first (apparent) and second saturation values is greater, and that, in the case

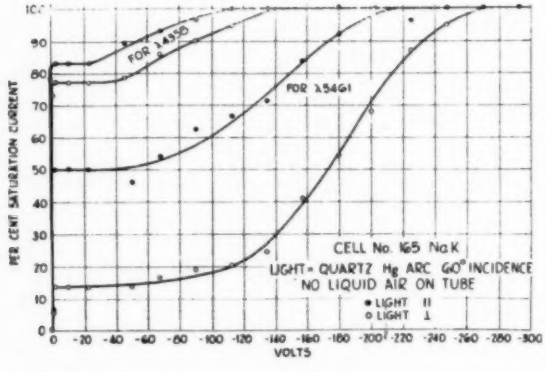

Fig. 10. Voltage-current curves for imperfect vacuum central cathode cell for ∥ and ⊥ light showing poorer saturation for ⊥ light.

shown, it is not possible even with liquid air to attain a vacuum sufficient to eliminate the second rise of current.

In Fig. 10 are shown data for ⊥ light and ∥ light in a cell without liquid air, for two wave-lengths of exciting light. The outstanding fact here is that,

as *judged by the saturation phenomena, the* ⊥ *light behaves as though it were of greater wave-length than the* ∥ *light.* Another feature of the influence of small quantities of gas is that the ratio of emissions (∥/⊥) is much greater for the low voltage saturation than for the high. This is exhibited again in Fig. 11 where the ∥/⊥ ratio changes from approximately 8:1 at zero volts to approximately 2:1 for 4 volts and above. Students of photoelectricity will recognize in Fig. 11 precisely the kind of curves obtained by Lenard[10] who ascribed the knick to a surface layer. Later work[11] has been interpreted as proving this corner at low voltages to be due to reflected electrons, but the dependence on gas pressure here shown is more in accord with Lenard's view.[12]

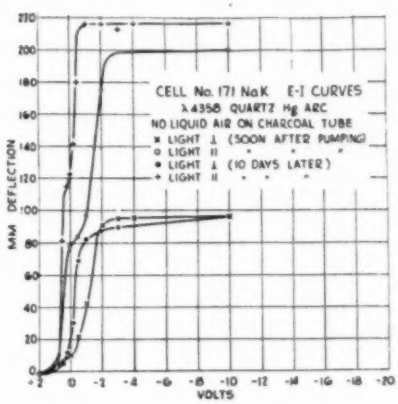
CELL No. 171 NaK E-I CURVES
λ4358 QUARTZ Hg ARC
NO LIQUID AIR ON CHARCOAL TUBE
× LIGHT ⊥ (SOON AFTER PUMPING)
○ LIGHT ∥ " " "
● LIGHT ⊥ (10 DAYS LATER)
+ LIGHT ∥ " " "
MM DEFLECTION
VOLTS

Fig. 11. Voltage-current curves for imperfect vacuum central cathode cell, showing poor saturation effect extending over voltage range of approximately 2 volts. Compare with Figs. 9 and 10.

We are not prepared to offer a detailed explanation of these effects of residual gas on the voltage-current curves. The curves of Fig. 9 are in general what might be expected if the surface were spotted with areas covered with gas to a considerable thickness. Such spots of gas would retard the slower electrons emerging from the metal surface beneath them more than the fast electrons, but the application of strong fields would ultimately pull the electrons through the retarding layer. According to this theory the initial saturation currents arise from the clean areas between the gas covered spots. If the data of Fig. 10 are to be interpreted as showing that the ∥ electrons are faster than the ⊥ then this is a property they possess only when the surface is gas covered, for as already shown by the data in Figs. 8a and 8b the voltage-current curves for the two kinds of light show complete similarity for the gas-free surface. In view of the additional complexity of the phenomena with long wave excitation in the presence of residual gas we have purposely restricted the present study to the conditions of high vacuum and short wave excitation, these being fortunately at the same time the conditions for the most definite exhibition of the differences of emission under ⊥ and ∥ light.

[10] Lenard, Ann. der Physik **8,** 149 (1902).

[11] Ladenburg and Markau, Ver. d. Phys. Ges. **10,** 562 (1908).

[12] The defects of saturation shown in Figs. 9 and 11 explain results obtained in certain earlier investigations. Thus in a study of central anode cells (Ives and Fry, Astrophysical Jour. **56,** 1 (1922)) it was found that the curves for "red" and "blue" light were not separated so far as the theory would indicate. It now appears that this was due to the relatively poorer saturation of the "red" current in the presence of residual gas. Again the announcement of a lower energy of emission for ⊥ electrons (Ives, Phys. Rev. **21,** 713 (1923)) was a misinterpretation of curves similar to those of Fig. 11, which, particularly in the presence of a "tail" of emission from the anode appear like similar curves shifted laterally by nearly a volt.

The next set of data in order for consideration are the voltage-current curves for individual tabs or collectors at various angular positions with respect to the cathode. In Figs. 12, 13, 14 and 15 are shown a set of curves

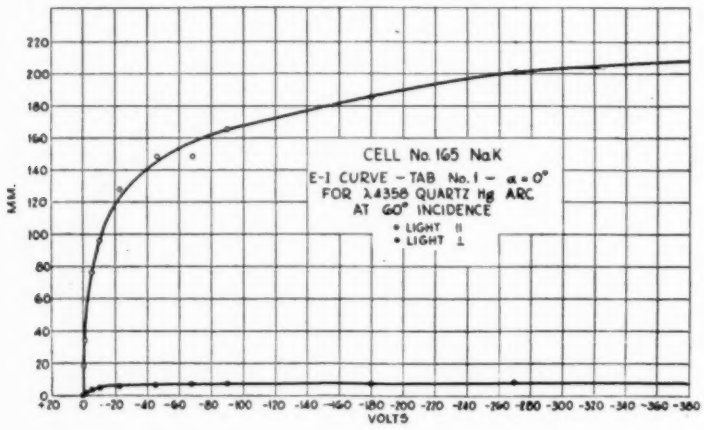

Fig. 12. Voltage-current curve to collector at normal to surface ($\alpha = 0°$).

for tabs at angles of 0°, 30°, 60° and 90°, which are representative of a great many obtained in the course of the investigation. The characteristic feature of the voltage-current curves for tabs at high angles to the normal is that the current rises quickly to a maximum for very low voltages and then declines,

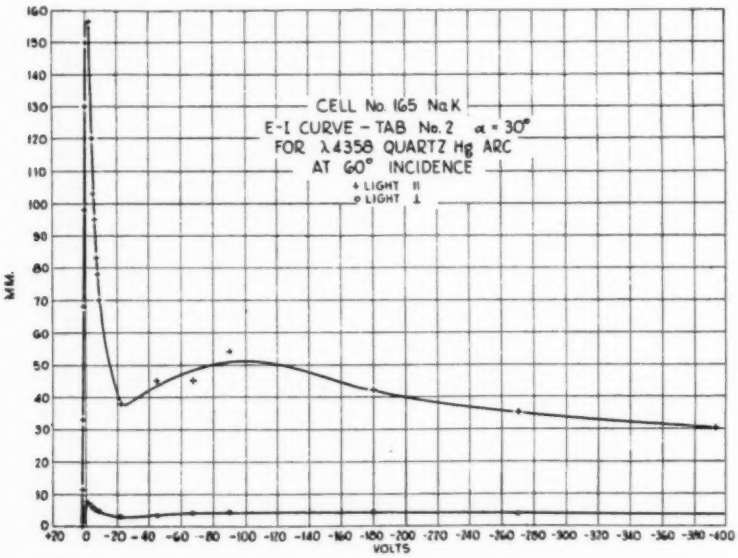

Fig. 13. Voltage-current curve to collector at 30° to normal ($\alpha = 30°$).

in excellent agreement with the calculated curves of the theoretical paper previously referred to. This agreement is in fact sufficiently close, as is shown by Figs. 16 and 17, to indicate that the underlying assumptions as to direction

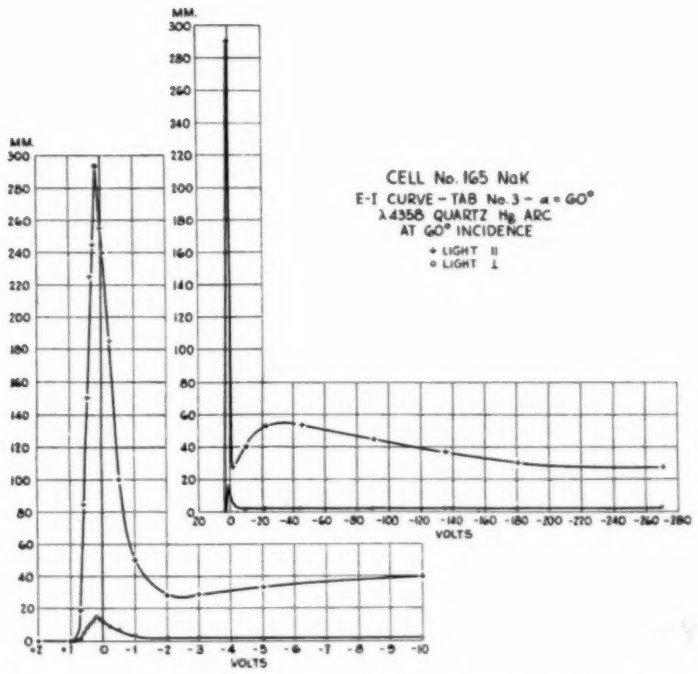

Fig. 14. Voltage-current curve to collector at 60° to normal ($\alpha = 60°$). Same curve plotted on two scales.

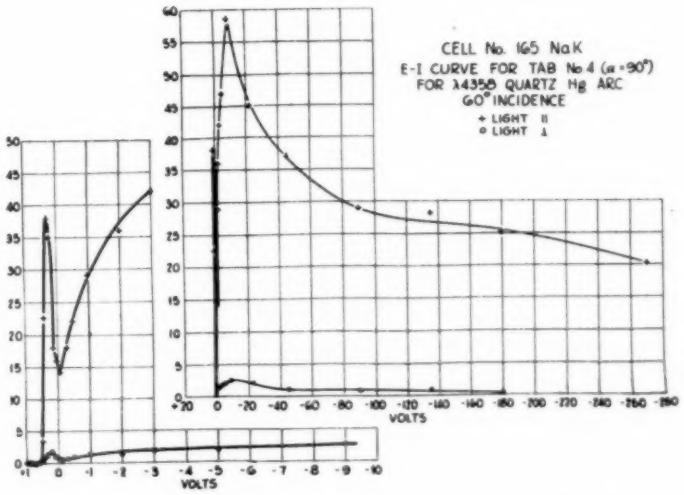

Fig. 15. Voltage-current curve to collector at 90° to normal ($\alpha = 90°$). Same curve plotted on two scales.

and velocity distribution used in the theoretical study must be very near the truth. It will be noted that in general the maximum current falls at the correct voltage and that the shape is closely similar to that given by the theory. Some of the differences which appear between the experimental and calculated curves are such as may be explained by the difficulty in determining the exact angle to be assigned to a finite tab, others to the finite size of the illuminated spot. The data shown in Figs. 16 and 17 suggest that there is an excess of high energy electrons at small angles to the normal and a deficiency at high angles. It is to be noted, however, that these observations

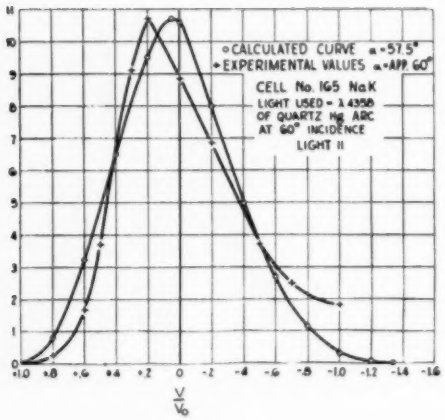

FIG. 16

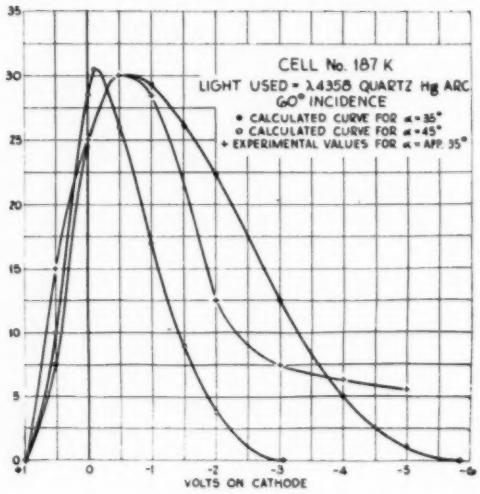
CELL No. 187 K
LIGHT USED = λ 4358 QUARTZ Hg ARC
60° INCIDENCE
• CALCULATED CURVE FOR α=35°
o CALCULATED CURVE FOR α=45°
+ EXPERIMENTAL VALUES FOR α=APP. 35°
VOLTS ON CATHODE

FIG. 17

Fig. 16. Comparison of calculated and experimental voltage-current curves for collector at 60° from normal to cathode. Failure to agree at peak is as expected since computed values (taken from preceding paper) are for slightly smaller angle.

Fig. 17. Comparison of calculated and experimental voltage-current curves for collector at approximately 35° from normal to cathode. Note how slight increase in size of angle moves curve to left.

were on flat electrodes, instead of the spherical one assumed in the calculations, so that exact agreement is not to be expected. Considering all our experimental data we find no sure evidence that the energy distribution differs for different angles of emission. This is of course a question which could be answered by experiments with other types of cells designed specifically for the purpose.

There is, however, a feature of these curves which is not in accord with the theory, and that is the behavior at higher voltages. Instead of falling as predicted to zero at some relatively low voltage, the emission approaches zero, rises to a second maximum and then again declines very slowly toward the highest voltages studied. This emission at higher voltages was the subject of very considerable study during the course of this work. It was at

first thought it might be a characteristic of the flat plate cathodes used in our earlier cells instead of the spherical cathodes assumed in the theoretical study. This led to the construction of several cells with a polished spherical platinum cathode on which the alkali metal was sublimed, as illustrated in Fig. 1. These cells gave exactly the same type of curves as the flat plate cells. It was then thought possible that the high voltage emission was caused by the platinum surface, in spite of its high polish, not being as perfectly specular as for instance a liquid sodium-potassium alloy surface. It was also thought possible that it was due to scattered light falling upon other parts of the electrode. To test these possibilities, cells were made up with a cup into which liquid sodium-potassium alloy was allowed to flow, and one of these cells was made with side tubes, one carrying the glass window to a considerable distance from the cathode, the other acting as a trap for the reflected light as previously described (Fig. 2).

The high voltage emission persisted in spite of these changes of design. As a result of our work we have, however, established that the unpredicted emission at high voltages is proportional to the principal electron emission as found, in agreement with prediction, at low voltages. This is shown by Figs. 13 and 15 in which the two curves for light in the $\parallel$ and $\perp$ planes are practically directly proportional to each other at all points. If the unpredicted emission were due to scattered light it would be substantially the same for $\perp$ and $\parallel$ light. We conclude from this proportionality that the high voltage current is due to secondary emission of electrons from the anode, as a whole, to the collecting tab. The shape of the voltage-current curve is in general agreement with this idea. For, as the voltage is increased from zero and electrons strike the anode at higher speeds, we would expect an increase of the secondary emission. On the other hand, with increasing field the primary electron stream is pulled more and more toward the normal to the surface, thereby restricting the emission of secondaries to a smaller spot on the anode, farther distant from the high angle collecting tabs. Due to this focussing of the primary emission we should expect a decrease in the number of secondaries striking the high angle tabs, and this decrease should set in earlier the higher the angle of the tabs. This is just what occurs, the maximum for the secondaries moving from 8 volts for the 90° tab to 100 volts for the 30° tab.

For our present purposes this secondary emission, once recognized as such is of no great importance, since in order to determine the distribution-in-direction it is only necessary to work at voltages of zero or less, where the secondary emission is negligible. Even were it appreciable, the fact that it is apparently directly proportional to the low voltage emission which we deem primary would tend to cancel its effect on our significant measurments.

Before passing on to the next type of data, we note that according to Figs. 12–15 there is no apparent difference in the character of the emission due to the $\parallel$ and $\perp$ kinds of illumination, when measured to individual tabs.

We are now ready to consider the direction distribution data, represented as to their general character by the ellipses of Fig. 7.

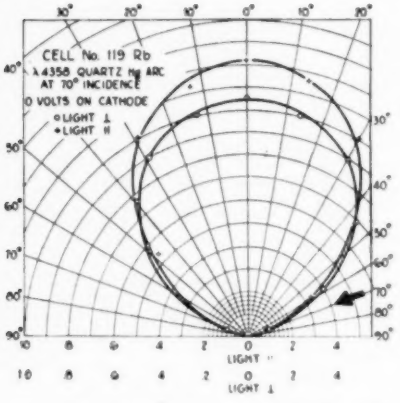

Fig. 18. Symmetrical angular distribution curve showing no tendency for electrons to follow electric vector of polarized light. Arrow shows direction of incidence of light.

The question of greatest interest perhaps with regard to these distribution curves is whether they reflect in any way the direction of the electric vector, as appears to be the case with photoelectrons produced by x-rays. In Fig. 18 are exhibited curves made with an exploring finger cell such as Fig. 1. In this the exposed end of the exploring finger rotates in an arc in the plane of incidence of the light, so that with obliquely incident light, if there is any following of the direction of the electric vector, the distribution curve should show a pronounced tilt for $\parallel$ light and no tilt for $\perp$ light. *Examination of these curves shows that there is no evidence of inclination of the ellipses.*

When this result was thoroughly established by a number of trials some study was made of the optical properties of metals to get an idea how much or how little tilt might be expected if the emission was due to light which had penetrated into the metal. The results of this study, which was made by Mr. T. C. Fry, are embodied in a recent paper by him.[13] In Fig. 17 of that paper will be found graphically represented the nature of the vibrations of the electric vector inside the metal. It appears that in all cases the ellipse by which the vibrations are represented is oriented with its major and minor axes very nearly tangential and normal to the boundary respectively, no matter how great the angle of incidence of the light. It might therefore not be considered surprising that the photoelectric emission shows no dissymetry with obliquely incident light.

It is however evident from Mr. Fry's work that if plane polarized light is *incident perpendicularly* on a metal surface, the electric vector keeps its direction unchanged in the metal. Consequently if when the plane of polarization is rotated the electron emission has a tendency to follow the electric vector, the ellipses of Fig. 18 should be much flatter when the electric vector is in the plane of collecting finger or tabs than when at right angles thereto.

This point was then tested experimentally. Light was incident on a sodium-potassium alloy surface in a perpendicular direction with the axis of the polarizing prism turned first to be parallel with the plane of the collector tabs and then at right angles thereto.[14] All the tabs were small and of the same size

[13] Fry, J.O.S.A. **16**, 1 (1928).

[14] This is our only experiment in which the $\perp$ light was passed through a polarizing prism.

for the cell used. The observed points are given in Fig. 19. These show that *there is no difference whatever in the shape of the curves as the plane of polarization is turned.* The conclusion must therefore be drawn that in photoelectric emission from the alkali metal surfaces tested there is no tendency for the photoelectrons, after leaving the surface, to follow the electric vector. *All the direction-of-emission curves obtained are symmetrical about the normal to the surface.*

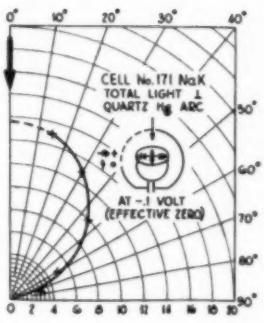

Fig. 19. Angular distribution curves for electrons emitted by polarized light at normal incidence. Result identical with electric vector of light parallel to and perpendicular to plane of collecting tabs. Small arrows show direction of light vector.

A practical advantage was taken of this result to build certain of the subsequent cells with the collecting tabs most distant from the normal several times the area of those near the normal, thus increasing the otherwise very small currents and securing greater accuracy in the measurements (Fig. 2).

Having disposed of this interesting question we may now examine in detail the distribution-in-direction curves, considering first their general shapes, and secondly the differences actually produced by changes in the nature of the illumination. It is first of all clear that the ellipses drawn through the experimental points in Figs. 5, 7 and 18, thus far referred to, are of the general shape called for by Lambert's law, previously assumed in our theoretical treatment. We may go further than this, however. If we examine Figs. 18 and 24 we find that in each case the ellipse for excitation by $\perp$ light is *accurately that called for by Lambert's law.* That is, in Fig. 18 where the cathode is a sphere concentric with the anode, the ellipse for $\perp$ light for zero field is slightly longer in the direction normal to the surface, just as it should be according to the calculations of the previous paper, which were made for a cell of this type. As pointed out, the true distribution (circle) would only be obtained for a small retarding potential. Again, in Fig. 24, where the cathode is a flat surface, with the emitting spot accurately in the center of the spherical anode, the curve for $\perp$ light is *accurately a circle.* While there are experimental curves for $\perp$ light among those shown subsequently, which are not exact circles for zero field, these were obtained under conditions where the exact determination of the effective zero field was not in question, or where the plane of the cathode was not so exactly central as in the cases shown. Hence we believe our data support the view that *Lambert's law is followed by the emission excited by $\perp$ light.*

We may now consider the differences in the emission curves, as the angle of incidence and plane of polarization of the exciting light are varied. Typical of our experiments on this point are the curves shown in Fig. 20, which are similar to a great number obtained with all the types of cells described for

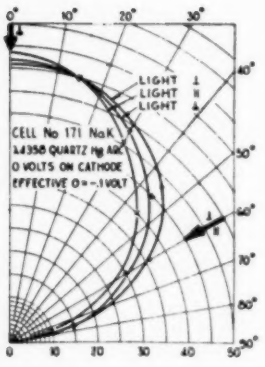

Fig. 20. Angular distribution of photoelectrons. Curves for light ∥, ⊥, ⊥̲. Effective zero $= -0.1$ volt, so cathode voltage for these curves $= +0.1$ volt.

⊥̲, ∥ and ⊥ light. They differ in that, regarded as ellipses, the ∥ curve is the most eccentric (longest axis normal to surface), and the ⊥ curve the least eccentric of the three, the ⊥̲ curve being intermemediate. The differences exhibited are indeed such as would be caused by a very small difference in the applied voltage, as is shown by Figs. 21 and 22, distribution-in-direction curves for various small retarding and accelerating potentials are plotted. (These are arbitrarily reduced to the same maximum value in order to exhibit the differences in shape more clearly.)

It is a matter of considerable importance to know whether the characteristic difference in shape for ⊥ and ∥ light is a function merely of the angle of incidence and plane of polarization of light or whether it is related to the actual ratio of emissions for the various optical conditions. In order to determine this point, it is necessary to have distribution curves for surfaces in which the ratio of emissions varies over a wide range. We have had no difficulty in the present study in producing surfaces in which the ratio of emission for ∥ and ⊥ light is as high as 20 to 1. We have, however, met with considerable difficulty in securing low ratios of emission. According to a

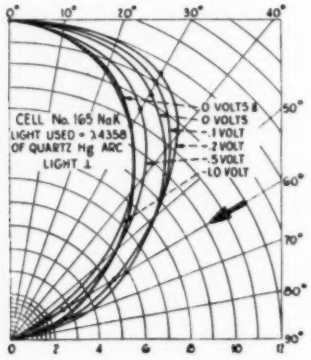

Fig. 21(a). Angular distribution of photoelectrons for light ⊥ with slight retarding potentials.

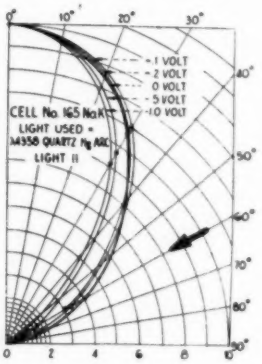

Fig. 21(b). Same as Fig. 21 (a) but for light ∥.

previous study[6] it should be possible, by choosing the relative proportions of sodium and potassium in the alloy to secure liquid alloys in which the ratio of emissions was as low as 2 or 3 to 1. Actually we have had very poor success, for the reason that alloys so prepared and exhibiting low ratios when measured in a side tube, would assume very quickly a relatively high ratio when subsequently flowed into the cup in the main tube. This we believe

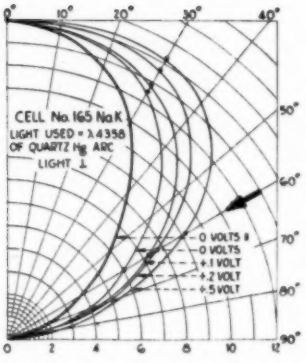

Fig. 22 (a). Angular distribution of photoelectrons for light ⊥ with slight accelerating potentials.

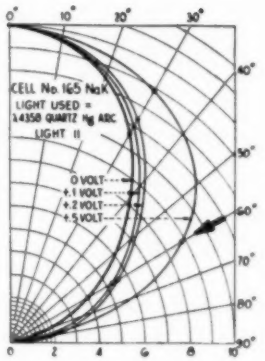

Fig. 22 (b). Same as Fig. 22 (a) but for light ∥.

to be due to the fact that it has never been possible in these large cells with their soot-coated anodes to secure and maintain the extremely high vacua which are necessary to prevent some contamination of the surface. As Fleischer[15] has shown, a pure potassium surface which initially has a low ratio will take up sufficient hydrogen from the walls of a supposedly well exhausted vessel to develop a relatively high ratio.

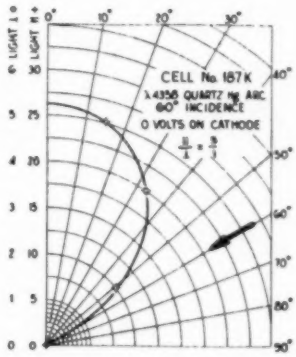

Fig. 23. Angular distribution of photoelectrons at 0 volts for pure potassium.

Our best data referring to a low ratio surface were obtained from a cell in which the cup was filled with pure solid potassium, which was allowed to cool slowly so that it developed a specular surface. In Fig. 23 the data for this cell, for which the ratio emissions for ∥ and ⊥ light was 5 to 1, are shown by the circles and crosses. The two curves in this case coincide in shape. Also in Fig. 24 are shown the data for a cell in which the ratio was of intermediate value, namely 19 to 1. The ellipses in this case are well separated, while in the curves of Fig. 25 for a cell in which the ratio was 23 to 1, they are still further apart. It must be recorded, however, that we cannot consider these data entirely satisfactory in view of the fact that the potassium surface, while specular, was somewhat uneven and not comparable in character with the liquid alloy surfaces. It is possible that the surface was sufficiently rough so that the coincidence of the curves for ⊥ and ∥ light is after all, in part at least, due to the occurrence of some ∥ excitation under all conditions. Such data as we have on this point appear to be consistent with the view that the increasing eccentricity of the ellipse representing the distribution-in-direction is a function of the ratio

[15] Fleischer, Ann. d. Physik **82,** 243 (1927).

of emissions for ⊥ and ∥ light but the data are not as full or conclusive as we could wish.

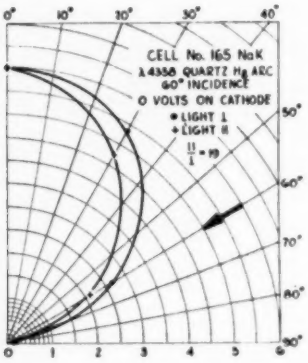

Fig. 24. Angular distribution of photoelectrons at 0 volts for Na K alloy. Ratio $\parallel/\perp = 19$.

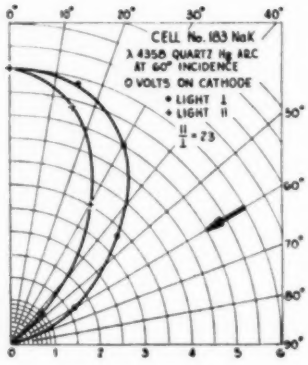

Fig. 25. Angular distribution of photoelectrons at 0 volts for Na K alloy. Ratio $\parallel/\perp = 23$.

Discussion of Experimental Results

The outstanding experimental results may be summarized as follows:

1. The distribution of photoelectrons in direction closely follows Lambert's law, the approximations being closest for excitation with obliquely incident light, with the electric vector parallel to the surface.

2. The distribution is under all conditions of illumination symmetrical about the normal to the surface.

3. The emission is more concentrated toward the normal for normally incident light than for obliquely incident light when the electric vector is parallel to the surface. The emission is still more concentrated toward the normal to the surface when, with obliquely incident light, the electric vector is parallel to the plane of incidence.

Another result is not so clearly established but may be stated as probable, namely:

4. The relative concentration of the emission toward the normal to the surface for obliquely incident light polarized in the two principal planes increases as the ratio of emission of photoelectrons for the two kinds of illumination increases.

It is now proper to attempt some explanation of the experimental findings in terms of the electrical or optical factors involved.

Any correspondence between the direction of emission, and the direction of the electric or magnetic vectors of the exciting light appears to be ruled out by our experiments. The close approximation to Lambert's law is most simply explained by assuming an entirely random direction of emissions within the metal, with a sufficient density of emitting centers so that the number passing through an element of surface in any direction will be as the projected area of the element in that direction. The explanation of the deviations we find from Lambert's law are then to be sought in some superposed or distorting effect, characteristic primarily of the surface, rather than of the exciting light.

One characteristic of the surface, deserving of consideration, is its work function. This might conceivably be altered by the character of the exciting light. As already stated, the differences in the direction distributions for $\underline{\perp}$ $\perp$ and $\parallel$ illumination are exactly those which would occur if the applied field differed in the several cases. As is shown by Figs. 21 and 22, a difference of a few tenths of a volt would suffice. In the case of gas contaminated surfaces (Fig. 10) a very considerable difference of voltage is actually required to release the second saturation electrons due to $\parallel$ and $\perp$ light, lending weight to the idea that a surface presents different opposing forces under the two conditions. However, for the case we are here concerned with, surfaces in the gas-free condition, the voltage-current curves for the total $\perp$ and $\parallel$ currents in Fig. 8, which are identical, give no support for an explanation calling for different effective fields in the two cases.

A second characteristic of the surface is its relative absorptive power for light incident at various angles and planes of polarization. Curiously enough —for it is difficult to interpret its significance—the one apparently complete correlation shown by our work is between the eccentricity of the ellipses representing the distribution-in-direction and the relative photoelectric emissions for the various illumination conditions. Thus the smallest emission is for $\perp$ light, the greatest for $\parallel$ light, with an intermediate emission for $\underline{\perp}$ light. In the case of $\perp$ and $\underline{\perp}$ light the emissions are practically as the absorption of light by the alkali metal. In the case of $\parallel$ light the emission is out of proportion to the absorption, as ordinarily measured, for infinitely thick layers, but may be proportional to the intrinsic absorption of a surface layer, peculiar to the occurrence of the "selective" effect. The correlation here pointed out is therefore probably between eccentricity and absorptive power. We have, however, been unable to find, by study of the optical properties of metals[13] any difference in the behavior of the differently absorbed kinds of light, such for instance as depth of penetration, which offered any clue to the meaning of this correlation. This correlation, it may be pointed out, is exactly opposite to that which would be exhibited by the surface if emitting thermal radiation. In that case, if the emitted radiation were examined in different directions, and for different planes of polarization, the deviations from Lambert's law would be in the opposite order.

Gardner in the paper referred to previously develops the idea that the photoelectrons, initially ejected in all directions equally, suffer absorption or loss according to the distance traversed in reaching the surface. This picture leads to a distribution-in-direction substantially according to Lambert's law. It further indicates that the greater the depth at which the electrons originate the more the emission will be concentrated toward the normal. If this theory were accepted the differences exhibited under $\underline{\perp}$, $\perp$ and $\parallel$ illumination could be explained by supposing that the average depth from which the electrons are extracted varies with the character of the light, being greatest with $\parallel$ light.

Against this view several objections may be raised. In the first place, as already noted, the electromagnetic theory of the optical properties of metals

does not permit of any significant difference in "depth of penetration" for the several kinds of light. In the second place, there is evidence[16] that the photoelectrically active layer is at most only a few atoms thick (<5), a depth at which optical absorption is insignificant. Another objection to the theory is that it pictures the electrons as continuing their initial direction of emission both inside and outside the metal, in spite of the encounters to which their diminution in numbers is ascribed. In other words, the electrons must be assumed either to emerge without any deflecting encounters, or to be completely stopped by every encounter. The distribution of electrons according to energy, which has often been ascribed to velocity losses after several collisions, would have to be assigned to some other cause, since such collisions would probably alter the paths of the electrons as well.

Disregarding for the moment the seriousness of these objections it is of interest to note that the differences in depth of penetration, i.e., in optical absorption, for $\perp$, $\parallel$, and $\underline{\perp}$ light called for if we assume the observed differences in emission to be due to this cause, are similar to those exhibited by a plate of tourmaline cut at right angles to its optic axis. While the structure of tourmaline is not known, it is probable that its markedly different absorption for light polarized parallel and perpendicular to the optic axis is due to a regular arrangement of atoms with very different spacings in different planes.

An alternative assumption to that of different depths of penetration is that there are present several kinds of atoms or atom groups, certain of which are capable of ejecting more electrons normally to the surface than others, and that these particular atoms or groups are at the same time more easily excited by $\parallel$ than by $\perp$ light. This assumption does not commit us to any simple relation between the direction of the electric vector and the direcl tion of electron emission, and is thus far in agreement with our experimenta- findings. It offers, however, no explanation of the intermediate character of the emission under normally incident light ($\underline{\perp}$).

While we have not been able to formulate a satisfactory theory for the distribution-in-direction phenomena we have observed, one common feature of the partial hypotheses just outlined appears to be inevitable in all attempted explanations of normal and selective effects. This feature is the assumption of some form of anisotropy of the surface, whereby it is distinguished from the isotropic or amorphous structure which ordinary measurements of the optical properties of the alkali metals indicate, and on which the calculations of absorption, reflection and other optical properties are ordinarily based. The fact that the photoelectric emission is due to an extremely superficial layer of atoms allows us to ascribe the peculiar properties under discussion with considerable confidence to some special arrangement of these atoms, even though the exact nature of this arrangement eludes us.

BELL TELEPHONE LABORATORIES, INC.
February 7, 1928.

[16] Ives and Johnsrud, J.O.S.A. & R.S.I.

RECENT LIGHT ON THE NATURE OF GASEOUS IONS

By Leonard B. Loeb

Abstract

The nature of gaseous ions from a study of mobilities in mixtures. After a general survey of the previous status of the question of the nature of the gaseous ion, it is concluded that for pure gases the dielectric attraction of the molecules by the charged ion can account for the order of magnitude of the mobility nearly equally well on either cluster or small ion theory. Such calculations are therefore indecisive. The measurements of mobilities in mixtures use Blanc's law as a criterion for the absence of the change of the cluster ion. The results show that Blanc's law holds in some cases and not in others. The observed nature of the mobility curves in mixtures shows three types of effects. These may be interpreted as indicating absence of clustering, labile clustering, stable clustering. The nature of the deviations in different gases indicates that where marked stable clustering occurs it is a specific effect depending on the chemical nature of the gas and sign of charge on the ion. Such effects are superimposed on the dielectric attractions mentioned above. Erikson's results on aging are discussed in their bearing on this work.

Introduction

IN THEIR initial paper on the electrical conductivity produced in air by x-rays, published in 1896, Rutherford[1] and J. J. Thomson stated that the observed mobility of the carriers studied was so much lower than the kinetic theory value for a charged molecule whose charge did not influence its motion through the gas by changing the paths of the molecules, that these carriers or ions were most probably composed of groups or clusters of molecules. Later measurements seemed to confirm this belief, which was generally accepted. In 1909 Sutherland[2] and Wellisch[3] independently stated that the shortening of the free paths necessary to explain the low observed mobility of gaseous ions could just as simply be imputed to the curvature of the paths of the ions and molecules as a result of the electrical forces between ions and molecules. These papers initiated a controversy which has continued with varying intensity up to the present. As is usual the discussion was carried on most violently by the extremists of both viewpoints and experimental evidence gained largely from the study of pure gases never seemed to be decisive. In recent times new evidence from the quantitative study of two previously neglected fields, that of the mobilities in mixtures and that of the mobilities as functions of the age of the ions, has given some very definite answers to the questions raised.

As is usually the case in such controversies, neither side was absolutely right nor completely wrong. Ions form clusters under some conditions ann probably do not form them under other conditions. Both types of actioy exist and exist together—hence the confusion. Although the results are faird

[1] Thomson and Rutherford, Phil. Mag. **42**, 392 (1896).
[2] W. Sutherland, Phil. Mag. **18**, 341 (1909).
[3] E. M. Wellisch, Phil. Trans. Roy. Soc. **A209**, 249 (1909).

convincing, many points yet remain to be cleared up and it may not be amiss to reformulate anew the gas ion problem in terms of what is known today, with the hope that this discussion will not only clarify the situation and therefore direct research in fruitful channels, but will also give rise to investigations of some of the phenomena yet obscure.

The Strict Cluster Theory

Shortly after the fundamental researches of Rutherford and Thomson and the careful experiments of Zeleny[4] on mobilities, attempts were made to deduce equations for the mobilities on the kinetic theory, using various lines of approach. Among those may be mentioned the theories of J. J. Thomson,[5] Riecke,[6] Lenard,[7] and Langevin.[8] These theories are based on an assumed cluster and leave the mass and the radius of the cluster undefined. As the mass factor for the ion plays a relatively unimportant role (the mass of the gas molecules present on the contrary being very important), the chief burden falls on the radius of the ion in these theories. It accordingly became the custom to assume that an undefined cluster existed and, by taking the observed value of the mobility together with the other factors, all of which were known, to compute a plausible radius of the ion which would satisfy this theory. Such a procedure is legitimate if the ion is a cluster and its radius as given by the theory is its real radius, that is to say, is not a radius that is in part due to attractive forces which alter its free path. Beyond this, however, the above method of approach is sterile, for it does not decide the question and leads to no further researches. It is, however, the point of view which has been taken by those strongly insistent on the strict cluster theory.

The Nature of the Forces Determining Ionic Mobilities

The more stimulating approach to this question is the one which asks whether it is possible, with known forces and properties of ions and molecules, to predict what will happen to a charged molecule moving among neutral molecules of dielectric constant D. Will, under such circumstances, the ion surround itself with a group of neutral molecules, or will it have its path merely altered in consequence of such forces? Finally do such forces suffice to give the approximate observed five-fold general decrease of the mobility of the ion below that of the theoretically computed mobility based on the equations cited above, if one assume a single charged molecule? Many such calculations have been made, although they have not been recently summarized.

In his recent book[9] on the kinetic theory the writer reviews the old idea that, with the inverse 5th power law of force which holds for dielectric

[4] J. Zeleny, Phil. Trans. Roy. Soc. **A195**, 193 (1900).
[5] J. J. Thomson, Proc. Camb. Phil. Soc. **15**, 375 (1910).
[6] Riecke, Wied. Ann. **66**, 376 (1898).
[7] P. Lenard, Ann. d. Physik **3**, 313 (1900); **60**, 329 (1919); **61**, 665 (1920).
[8] P. Langevin, Ann. de Chim. et de Phys. **28**, 317 (1903).
[9] L. B. Loeb, Kinetic Theory of Gases, McGraw-Hill, New York, 1927, p. 455.

molecules attracted by a charge, the condition for stability of an ion cluster is that the ratio of the potential energy W to the kinetic energy $K.E.$ given by

$$W/K.E. = (D-1)e^2/12\pi p\sigma^4,$$

is equal to or greater than unity. If the usual values of the quantities are chosen for the case of air, $W/K.E.$ is found equal to about three. This indicates the possibility of a cluster formation. Nevertheless the value of $W/K.E.$ is so critically dependent on the unknown distance σ between the charge of the charged molecule and the molecules attracted in the cluster, and the laws of force on dielectric molecules are so little known at distances comparable with molecular radii, that we cannot with certainty assert that a cluster will form in any given case.* We may conclude from this that cluster formation is possible in air and may even be probable in HCl, but that in any case a cluster formed on the basis of this law is probably limited to a monomolecular layer of molecules surrounding the charged molecule. That is, the ion is limited to about thirteen molecules all told and possibly less, because twelve spherical molecules are all that can surround a single spherical molecule of like radius, and the radius required for a second monomolecular layer makes the cluster consisting of two molecular layers surrounding the molecule improbable.

Some workers[11] have attempted to superimpose on these electrical forces the van der Waals attractive forces of cohesion and thus obtained much larger clusters. While this is possible the writer agrees with Professor J. Franck in a recent discussion of the subject, that after all the electrical forces cannot be superimposed on the van der Waals forces, inasmuch as both are of the same nature (i.e., electrical) and it is probable that the van der Waals forces will be replaced by electrical forces, of a different nature produced by the ionic charge.

It must also be borne in mind that if a cluster forms under this law of force, the ion so formed will still act on neutral molecules beyond the confines of its own cluster with electrical forces in such a way as materially to change their free paths. Thus even a cluster of the electrical nature outlined above must in part act like a small ion.

One more conclusion may be drawn from this theory. It has been shown by Langevin that in the recombination of two ions[12] attracting each other according to a law of force in which $W/K.E. = 2e^2/mv^2r$ and in which the forces are many times larger than above, the ions do not recombine whenever they collide, but that there is a large chance that they will again separate even at atmospheric pressure. This follows from the dynamics of the process of recombination. It is therefore to be expected that the chance that a molecule which is attracted to an ion by a vastly smaller force will have a

* In spite of the question above concerning the validity of the dielectric laws of attraction in the intense radial fields of ions at molecular distances, Debye[10] has shown that the law appears to hold surprisingly closely.

[10] Debye and Hückel, Phys. Zeits. **24**, 205 (1923).

[11] A. P. Alexeievsky, Phys. Rev. **27**, 811 (1925).

[12] L. B. Loeb, Kinetic Theory of Gases, p. 483.

much smaller chance of attaching to the ion to form a cluster. This low probability of attachment is naturally counterbalanced by the very much greater number of impacts which the charged molecule has with neutral molecules. It must however be recognized that this situation may lead to a relatively slow formation of the ion, such that it might be conceivable that the ion cluster would require periods of the order of a thousandth of a second in a gas at atmospheric pressure to form itself by attachment of molecules.

It may well be asked whether the same forces, do they not cause a clustering, could give the proper order of magnitude to the mobility on the basis of a small ion concept, i.e., a single charged molecule. This question can be answered in the affirmative by citing a small ion theory first developed by Wellisch in 1909[3] and later modified by the writer,[13] or a theory independently developed by the writer[14] which he later found to be a special case of the more complete theory of Langevin.[15] The theory of Wellisch which was the first theory which from known physical quantities without arbitrary assumptions as to the size of a cluster gave mobilities of the observed order of magnitude, is based on the decrease of the free path caused by the attractions between ions and molecules, using the law of dielectric attraction cited above. The values from this theory as modified by the writer are quite successful, both in general magnitude and the order in which the various gases follow.

More interesting in a sense than the theory of Wellisch, though a theory which is definitely in error, is the theory of the writer based on a rigorous calculation of the changes of path resulting from an analysis of J. J. Thomson,[16] using the dielectric law of force. In this theory the ion is considered as a *point* charge moving in a gas of dielectric constant D and molecular weight M_0. The mobility is given by

$$K=\frac{0.104[(M+m)/m]^{1/2}}{(\rho/\rho_0)[(D-1)_0 M_0]^{1/2}},$$

where m is the mass of the ion, M the mass of the molecule, while ρ is the density and ρ_0 is the density for N.T.P. The constant term is questionable, because of the process of averaging, and m is unknown. The factor containing m changes the mobility by 40 percent for infinite mass so that it is not important. This equation again gives the mobility in order of magnitude for all gases fairly successfully, deviations by a factor of two at most being present. It is also interesting insofar as the theoretical mobility varies as nearly as the results warrant, according to the observed experimental data, being independent of temperature, the mass of the ionized molecule, and depending largely on D and M_0. The mobility in this equation is independent of the charge in contradistinction to the case of a particulate ion, such as one would have in the case of a Millikan oil drop. The theory therefore is interesting, as it furnishes an extreme type of theory of ionic behavior. This leads

[13] L. B. Loeb, Kinetic Theory of Gases, p. 456 ff.
[14] L. B. Loeb, Kinetic Theory of Gases, p. 460 ff.
[15] P. Langevin, Ann de Chim. et de Phys. **5**, 245 (1905).
[16] J. J. Thomson, Phil. Mag. **47**, 337 (1924).

one to see that as the radius of the ion is less and less dependent on the charge, the mobility varies more nearly in proportion to the value of the charge. As stated the theory however is definitely wrong in neglecting the molecular radius, but it serves to show how insensitive the mobility is to the radius of the ion in the presence of electrical forces. In this respect the theory is analogous to the Debye theory of ionic mobility in solution.

The More Complete Electrical Theory

The closest approach to the mathematical solution of the ion problem today extant is the one due to Langevin[15] in 1905, who using the above law of force calculated from rigorous kinetic theory the mobility of an ion of radius σ. This theory was assailed by Mayer[17] on the ground that it neglected the velocity of the ion in the direction of the field on a single free path. According to Mayer, had Langevin taken account of the velocity in the direction of the field, he would have obtained a mass factor in his theory which agrees with the mass factor noted by Lenard[7] on a strict cluster basis. Inasmuch as most measurements are carried out under conditions fulfilling Langevin's assumption, it seems hardly worth while to alter the theory, since the change in mass factor alters the mobility far less than many other factors. One may therefore accept the complete equation of Langevin as later developed by Hassé,[18] as being the most complete theory to date. It unfortunately leaves one with an undetermined radius and consequently makes it another arbitrary equation.

Conclusions from the Theoretical Considerations

The conclusions to be drawn from these considerations are as follows:

(1) The inverse 5th power law of dielectric attraction suffices for the calculation of mobilities of ions of the correct order of magnitude for ions either of the small ion type or of the cluster type.

(2) The laws so deduced agree as far as we can determine from the experiments equally well with either theory if pure gases are used, though such a comparison between the two points of view is difficult, as the ionic radius chosen in the case of the cluster theory is more or less arbitrary.*

[17] H. F. Mayer, Ann. d. Physik **62**, 358 (1920).

[18] Hassé, Phil. Mag. **1**, 139 (1926).

* This is not quite true in such extreme cases as the forceless cluster or the point charge. For the former the mobility is inversely proportional to the square root of the absolute temperature if the cluster size is not a function of temperature. For the latter the mobility is independent of temperature. It is probable that some other law for the variation of mobility with temperature, such as that of Sutherland[2] holds. Experiments on this point differ so widely that no conclusion can be reached. Phillips[19] claims to have established the Sutherland equation as does Schilling.[20] The equation as applied to a cluster ion exerting forces at constant density reads:

$$k_T = K_0\left(\frac{273}{T}\right)^{1/2}\frac{A}{1+C/T}$$

where K_0 is the mobility at N.T.P., T the absolute temperature, and A and C are constants. The work of Phillips is in disagreement with that of Kovarik,[21] done under the same conditions; and both are in disagreement with the careful work of Erikson.[22] The results of Schilling

(3) Doubtless both types of action occur and in some cases simultaneously. In this case the theory which is most nearly correct is that of Langevin. It is also likely that in some cases the cluster action predominates and in others the small ion action predominates. Thus *in order of magnitude ordinary forces of the dielectric type suffice to account for the mobilities, the nature of the ion and its mobility being undetermined* as far as crucial experiments in pure simple gases can ascertain. We must therefore turn to investigations in other fields to determine the nature of the ion.

Work on Mobilities in Mixtures of Gases

The first of the fields to be discussed, that of the mobilities in mixtures, presents because of the rather more complete control of experimental conditions, possibly the best line of approach. The study of the mobilities in mixtures began with Blanc[23] in 1908 for mixtures of gases H_2, CO_2, and air. He found that for these gases the law of mixtures to be developed below held quite well. To deduce the mobilities of the gases in the mixtures, it must be remembered that in analogy to the electrical conductivities, electrical gas ion mobilities in mixtures cannot be added. The reciprocals of both of these, that is the resistances to the current or to the motion of the ions, have however the additive property. Since the resistances are directly additive and the mobilities are inversely proportional to the densities of the gases, i.e., to the number of molecules present, the product of the reciprocal of the mobility in a given gas by its mol fraction can be added to the similar products for the other gases present and will equal the resultant resistance for the mixture. Thus dealing with binary mixtures at atmospheric pressure, consisting of c atmospheres of the gas a whose mobility is k_a and resistance $R_a=1/k_a$, and $(1-c)$ atmospheres of a gas b of mobility k_b and resistance $R_b=1/k_b$, we can at once write the resistance $R_c=1/k_c=R_ac+R_b(1-c)$. This leads to the mobility in the mixture expressed by the relation

$$k_c=\frac{k_ak_b}{(1-c)k_a+ck_b},$$

which is Blanc's law. The law applies within the limits of experimental error to an early measurement made by Wellisch[24] on a mixture of C_2H_5I and H_2 in 1909. These constituted all the complete, accurate measurements until more recent years.

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cover but a small range and as satisfactorily fit one theory as another, so that we cannot judge by these. If the Sutherland law should hold, the action is one based on a small ion type of action, since Sutherland's theory is based on the effect of the temperature on the free path of particles attracting each other according to some law of force. Erikson's work, which seems to be the most careful and covers a large range of mobilities, indicates independence of mobility on temperature, except near the liquid air temperature where the mobility is slightly decreased.

[19] P. Phillips, Proc. Roy. Soc. **A73,** 167 (1906).

[20] H. Schilling, Ann. d. Physik **83,** 23 (1927).

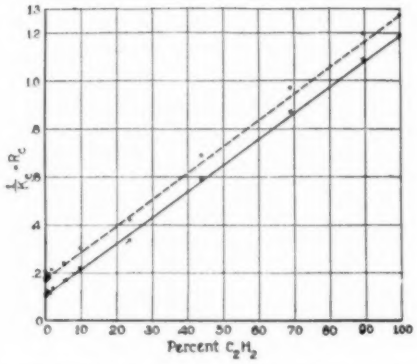
[21] A. F. Kovarik, Phys. Rev. **30,** 443 (1910).

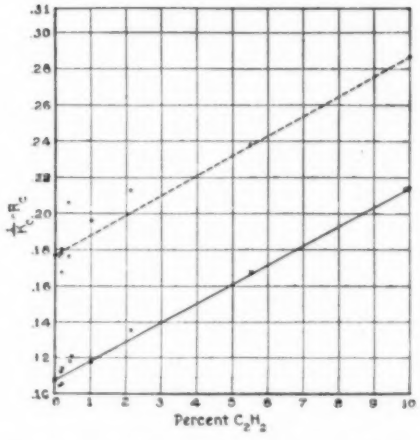
[22] H. A. Erikson, Phys. Rev. **3,** 151 (1914); and **6,** 349 (1915).

[23] A. Blanc, Jour. d. Physique, **7,** 825 (1908).

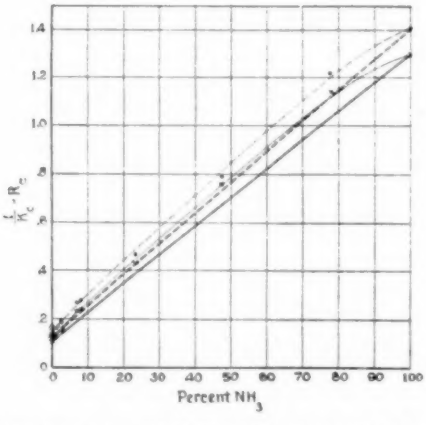
[24] E. M. Wellisch, Proc. Roy. Soc. **A82,** 500 (1909).

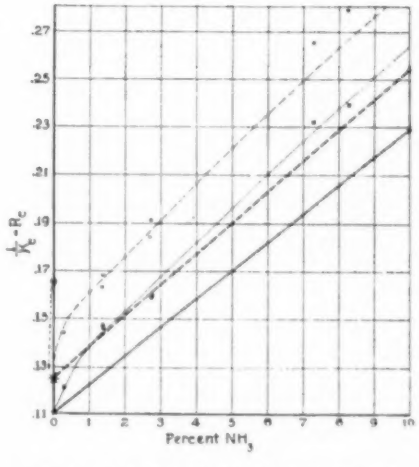
Although it had been repeatedly asserted that traces of water vapor and Cl_2 abnormally decreased the value of k for negative ions in air, to the writer's knowledge no careful quantitative studies of the mobilities over any





Figs. 1 and 1a. Mobility of ions in C_2H_2-H_2 mixtures. Reciprocal of mobility is plotted against percent of C_2H_2.





Figs. 2 and 2a. Mobility of ions in NH_3-H_2 mixtures. Reciprocal of mobility is plotted against percent of NH_3.

considerable range were made until about 1924. Since that time the writer,[25,26] Tyndall and Phillips,[27] and H. Mayer[28,29] have extended the

[25] Loeb and Ashley, Proc. Nat. Acad. Sci. **10,** 351 (1924); and Loeb, Proc. Nat. Acad. Sci. **12,** 35 and 42 (1926); ibid. **12,** 617 and 677 (1926).

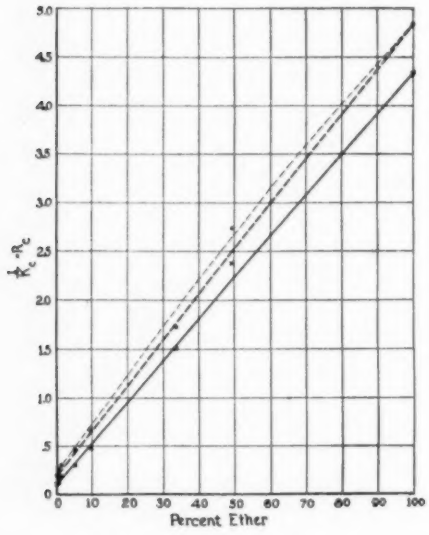
[26] Loeb and DuSault, Proc. Nat. Acad. Sci. **13,** 510 (1927); **14,** 193 (1928); and **14,** (1928) (in press).

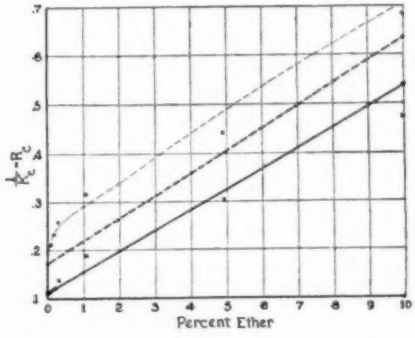
[27] Tyndall and Phillips, Proc. Roy. Soc. **A111,** 577 (1926).

[28] Herbert Mayer, Phys. Zeits. **27,** 513 (1926); **28,** 637 (1927).

[29] Herbert Mayer, Bulletin Faculty of Sciences, Cernauti, Roumania, Vol. II, No. 1, p. 65.

literature to a large number of mixed gases. The results of these investigations may be summarized in three types of curves. Typical curves representing these types taken from experiment are shown in Figs. 1, 2, 3, 4, 1a, 2a, and 3a. For purposes of comparison it is simpler to plot the curves for





Figs. 3 and 3a. Mobility of ions in ether-air mixtures. Reciprocal of mobility is plotted against percent of ether.

the mixtures in terms of the resistance, as these in the case of Blanc's law give a straight line, and deviations from a straight line very clearly indicate deviation from Blanc's law. In Figs. 1 and 1a the results for a C_2H_2-H_2 mixture of the writer's for positive and negative ions are given, showing the linear form characteristic of the strict Blanc's law in mixtures. In Figs. 2 and 2a the results for NH_3-H_2 mixtures are shown, the straight lines being the theoretical curves for Blanc's law following from the observed mobilities in pure hydrogen and NH_3 and the star representing the beginning of the positive ion curve in NH_3, indicating the observed mobilities in almost pure hydrogen after a trace of NH_3 had been admitted to the chamber. The third and fourth figures give the results for ether-air mixtures and for HCl-air mixtures, the solid line curve in each case referring to the negative ion, the other curve referring to the positive ion. In each case the calculated linear Blanc's law expression is included in the figure.

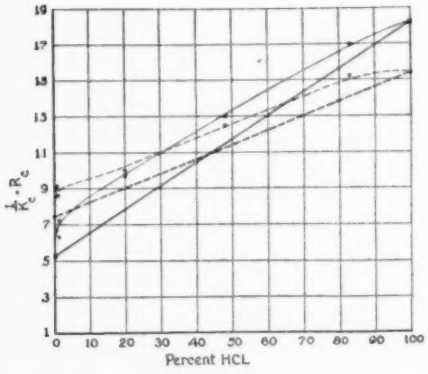


Fig. 4. Mobility of ions in HCl-air mixtures. Reciprocal of mobility is plotted against percent of HCl.

PREDICTIONS FROM THEORY AS TO MIXTURE CURVES TO BE EXPECTED

Before interpreting these results it seems advisable to study the two theories to foresee if possible what is to be expected.

(1) On the small ion theory since the mobility is inversely proportional to the density and the forces are exerted on the gas molecules as the ion encounters them, Blanc's law would be expected to hold and should characterize, where strictly obeyed, a small ion type of behavior. It seems that the Blanc law is probably as nearly definite a test of the small ion type of activity as possible, provided the ion does not in any way change the concentration of molecules about it.

(2) It is possible that with either cluster or small ion the forces on certain of the more actively attracted gas molecules resulting from high dielectric constant might change the concentration of the molecules in the neighborhood of the ion. It was shown by Condon[30] on the basis of the law of equipartition of energy, that such a local change in density of HCl in air was to be expected. In how much such a change of density can alter the mobility it is impossible to say, inasmuch as the change, no matter how reckoned, introduces only a partial increase in the drag on the ion by interaction with such molecules, since the molecules near the ion are already moving more or less in the same direction as the ion. An empirical relation only partially satisfied was found by Loeb[25] and Mayer[28] in certain mixtures. This equation

$$k_c = \frac{k_a k_b}{[(1-c)k_a^2 + ck_b^2]^{1/2}}$$

in the resistance form indicates an effect of such a nature as pointed out by Debye.[25] It is conceivable, however, that this relation may be explained in other ways.

(3) On the strict cluster concept in which the forces around the charged molecule vary greatly in their action on the two constituent molecules of the mixture, Blanc's law would hardly be expected to hold. Immediately a trace of the more active gas were admitted to the mixture this would selectively go to the ion to change its constitution; and *if the mobility depends on the size of such an ion*, the mobility should change abruptly to lower values which might be expected for a cluster of the more active gas. This means that low concentrations of the more strongly attracted gas should cause the mobility to drop and the resistances to the ions to jump upward very sharply, a marked deviation from the linear relationship being observed for low concentrations of the active gas. It is of course conceivable that the time consumed in the reconstitution of the ion might be fairly long, such that if the ion were measured in such cases very shortly after the ionizing act, the lowering effect to be expected would not have had time to occur and the mobility would appear to be unaffected by this gas.

(4) On a less rigid interpretation of the cluster theory, which one might expect on the basis of the electrical forces between ions and molecules, in

[30] L. B. Loeb, Kinetic Theory of Gases, p. 472.

which important forces are exerted beyond the immediate region of the cluster and where the cluster is more or less statistical in nature, it is to be expected that the cluster would adapt itself more or less readily to the average mixture. On this assumption it is probable that a more or less close approximation to the Blanc law would occur. If, however, there is some definite clustering it seems unlikely that the Blanc law would be obeyed with any accuracy and the same sort of deviation described under Paragraph 2 and illustrated by the curve of Fig. 2 might be expected.

Conclusion from the Mixture Experiments

These three types of behavior are illustrated by the schematic curves drawn in Fig. 5, the Curve (1) representing the resistance law, Curve (2) the deviation from the resistance law to be expected on either an increase of concentration effect for a small ion or for a labile ion, and (3) a typical curve indicating a marked cluster formation. Comparison of Fig. 5 with Figs. 1, 2, 3, 4, 1a, 2a, and 3a at once indicates that all types of action have been observed in only four mixtures mentioned. The mixture work may be summed up in terms of these factors as follows.

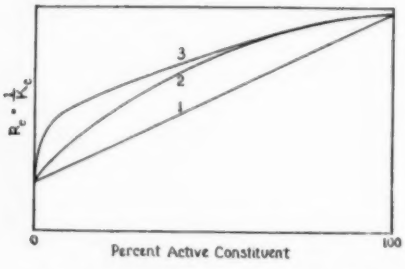


Fig. 5. Variation, anticipated from different ion theories, of mobility with concentration of the active constituent in a mixture.

(1) In mixtures of C_2H_2-H_2, CO_2-H_2, O_2-CO_2, C_2H_5I-H_2 and negative ions in ether-H_2 mixtures, Blanc's law is followed. In these one may properly assume no apparent clustering. If, as is likely, the final positive ion in air, CO_2 and H_2 is already a bimolecular cluster, as indicated by Erikson, this clustering is inherent in one or both of the gases and is not changed by the mixture. This could also be true for the negative ion, though it is less likely in view of the aging effect (see later). If in one gas, however, the positive ion clustering suggested by Erikson is replaced by another complex, we would see the abrupt change in mobility resulting.

(2) In mixtures of NH_3-H_2, NH_3-air, SO_2-H_2, the part of the HCl-air curves for *higher* concentrations of HCl, and in Cl_2-O_2 mixtures for positive ions, deviations from the Blanc law of the indeterminate nature mentioned in Classes 2 and 4 and illustrated in Fig. 2 and Curve (2), Fig. 5, occur. This will be due to a statistical labile cluster or to some concentration effect mentioned above, which amounts to the same thing.

(3) All other gases examined, negative ions in Cl_2-H_2 and Cl_2-O_2, Br_2-H_2, HOH and ROH-air mixtures, positive ions in ether-H_2 mixtures, and positive and negative ions in HCl-air and H_2S-H_2 show the definite clustering behavior unmistakably, HCl showing it over and above the concentration effect prominent at higher pressures of HCl.

There can therefore be no doubt concerning the cluster formation in some gases, while in others it is quite unlikely that clusters form. Probably

the most striking proof in this direction are the cases of ether, SO_2, and NH_3 in H_2 gas. The positive ion in ether shows indubitable clustering, while the negative ion shows no deviation from the Blanc law within experimental error. In NH_3-H_2 and SO_2-H_2 the NH_3 or SO_2 first admitted *increases* the mobility of the positive ion to nearly the value of the negative ion, after which both ions behave according to a law of an indeterminate type indicating a labile cluster or changes in concentration. In SO_2-H_2 mixtures[26] the positive ion shows this effect even more pronouncedly. One experiment on a mixture of ether, NH_3 and H_2 indicates that ether acts more strongly on the positive ion than NH_3, where present in equal quantities, so that the ether cluster or addition product is the more stable.

One more interesting fact is brought out by Tyndall and Phillips[27] in a study of the mobilities of positive and negative ions in a homologous series of alcohols ROH mixed with air. Here starting with water the deviations from the resistance law at very low concentrations of the vapors progressively decrease k more and more effectively. Since in general properties (i.e., the dielectric constant, vapor pressure, etc.) these vapors are more or less similar, the difference must be attributed to the size of the R group or chain of the alcohol added. This effect is not surprising inasmuch as the large size of the R group even if one molecule only were added would materially change the radius of the ion, and thus the sudden lowering will be the more effective, the greater the molecule attached. The mobilities at atmospheric pressure for these ions are all more or less nearly the same. We must therefore add to the consideration of the clustering the importance of the size of the molecules attached, in discussing the influence on the mobility for low concentrations.

Evidence from Aging Effects

The second line of evidence comes from the pioneer work of Erikson.[31,32] In spite of objections to these experiments to be mentioned, there are certain facts which cannot be neglected and which point to conclusions similar to those drawn from the mixture work. Erikson uses an air blast method which enables him to measure velocities at atmospheric pressure for ions very soon after the ionizing process takes place. He observed that independently of the age in all gases examined the negative ion retained a nearly constant k to within 0.002 seconds after formation. The positive ions at the shorter time interval have a k equal to that of the negative ions, but change to the lower values usually observed for positive ions in time intervals less than 0.03 seconds. The change is evidenced, on varying the age, by two definite peaks, the area under which varies relatively as the ions grow older. This occurs in such a manner that at the shorter time interval the one curve having the same mobility as the negative ion is all that is observed, but as the age of the ions is increased the second curve corresponding to the slower ion develops in area at the expense of the first curve and eventually, after 0.03 seconds,

[31] H. A. Erikson, Phys. Rev. **20,** 117 (1922); **24,** 502 and 622 (1924).

[32] H. A. Erikson, Phys. Rev. **26,** 465, 625, and 629 (1925); **28,** 372 (1926); **30,** 339 (1927).

comprises all the positive ions observed under its single peak. The age is varied by introducing the ionizing source in the gas at various distances from the measuring field. The existence of two independent peaks comprising all the ions has only one interpretation: the initial positive and negative ions are characterized by nearly the same value of k, while a slower type of stable positive ion develops after some time in the gas. There are therefore two distinct types of positive ions with no intermediate forms of any marked stability existing between them. The change of the mobility of the positive ion must therefore be regarded as a single step process. The simplest interpretation is that given by Erikson, who believes the negative ions to be monomolecular, as are the initial positive ions, while the aged positive ions have added another molecule to form a bimolecular ion. It could also be that the initial negative and positive ion are polymolecular and that the positive ion changes to a still more complex polymolecular form in a single process after a sufficient lapse of time.

While these results are fairly definitely established it must be stated that they have not been unquestionably verified experimentally either by another observer* or by using different methods. H. B. Wahlin[33] believed he had verified the effect using an alternating current method. The results of Wahlin were questioned by the writer[34] on a theoretical basis, and neither the writer nor Mr. Cravath, working in the writer's laboratory, was able to confirm the effect, although they seriously tried to find it with their methods. Tyndall and Grindley[35] also claimed to have verified the phenomenon of aging, using a modified A.C. method. They did not simultaneously observe the two types of positive ions and the experimental data reported are so meager as to be unconvincing.

Erikson has also observed many other curious effects, some of which are in agreement with observations of the writer in mixtures, while others appear to be exceedingly difficult to explain in any manner. The observations with ammonia in air confirm the experiments of the writer. The observations in which Cl_2 and H_2O added to the main body of the gas failed to produce the lowering of the negative ion mobility observed by other workers on older ions, could be explained on the hypothesis that the time spent in these gases in the high fields is too short to permit the negative cluster formation. The mobilities of high value observed for the radioactive recoil atoms of radium A, actinium A and thorium A, which apparently show no aging effect, are very difficult to explain. The high value of the positive mobility cannot possibly be explained by a double positive charge, but would require a triple or quadruple charge on the ion. Such a charge might be possible after disruption of the nucleus by an effect such as observed by Auger in the case of photoelectrically ionized atoms from short wave-length x-rays.[36]

* Since this paper was written J. J. Mahoney in the writer's laboratory has completely confirmed Erikson's results in air. (May 27, 1928.)

[33] H. B. Wahlin, Phys. Rev. **20,** 267 (1922); Proc. Nat. Acad. Sci. **10,** 475 (1924).

[34] L. B. Loeb, Proc. Nat. Acad. Sci. **11,** 428 (1925).

[35] Tyndall and Grindley, Proc. Roy. Soc. **A110,** 358 (1926).

[36] L. B. Loeb, Science **67,** 468 1928.

The most difficult of the observations to explain is the effect of C_2H_2 mixed with the ionized air in changing the mobility of the aged positive ion in air to the unaged positive ion in C_2H_2. The explanation on the basis of a cluster formation which has a higher mobility than the positive ion in air is completely negatived by the writer's experiments in C_2H_2-H_2 mixtures.[26] Erikson's explanation on the basis of the transfer of the charge from O_2 to C_2H_2, which might be expected in the light of the work of Franck and Cario, is not entirely satisfactory. It would force one to assume that the charged C_2H_2 molecule is incapable of forming an addition product or bimolecular cluster with foreign molecules, while the positively charged oxygen molecule can do so. As far as evidence goes, the nucleus has little influence on the cluster while the charge and the surrounding gas molecules are very important.

Another effect observed by Erikson in H_2 and in C_2H_2 in which the initial positive mobility was slightly less than the initial negative mobility, can receive a simple explanation suggested by the writer[26] on the basis of the fact that Erikson measures his mobilities so soon after ionization in gases like H_2 and C_2H_2, where the electron does not attach except to impurities, that it is probable that the high values are due to the initial presence of electronic carriers in these gases. This is confirmed as a result of the writer's own studies on the existence of free electrons in both H_2 and C_2H_2, even though slightly impure, when the mobilities are measured within short time intervals.

These more complicated results have not been discussed in as much detail as they possibly warrant, inasmuch as the writer feels that in its present state the Erikson method has sufficient uncertainties as not to give one the utmost confidence in the more unusual results. The chief uncertainties apparent to the writer may be summed up under the four heads below.

(1) The air-blast method as used *does not permit of much control of the purity of the gas.* This the writer's work on mixtures has shown to be of the greatest importance.

(2) The effects of the high fields on the values of the mobility are unknown. While this fact does not influence the important results of Erikson quoted above, inasmuch as they depend for aging on processes independent of the field and on relative mobilities, it is still important that these effects be understood and controlled.

(3) An air blast method is distinctly unsuited for the measurement of true absolute mobilities, and it is a natural tendency to standardize such an apparatus in terms of the mobilities in air and assume that this standardization is applicable in the case of other gases. *It is essential that the absolute values of the mobilities, as nearly as it is possible to get them, should be determined directly in almost every set of measurements.* An instance of the importance of such standardization may be cited by the hypothetical case to be detailed. In the presence of water vapor where the negative mobility is depressed relative to the positive mobility, an apparent relative change in the positions of the aged positive peak and the negative peak might seriously confuse the conclusions to be drawn. Doubtless in Erikson's experiments precautions

of this type were always taken, but their importance cannot be overemphasized.

The criticisms not withstanding, the results of Erikson all in all indicate a type of cluster formation which is in general agreement with the conclusions drawn from the results on mixtures. They are cogent in that they indicate the *unitary* nature of the change of mobility of the positive ion and emphasize the *time element* in the process.

The Difference in Positive and Negative Mobilities and Final Conclusions

It is now essential to go one step further and investigate the difference of positive and negative ion mobilities, a difference not to be expected on the simple assumption of dielectric forces of attraction. This difference of the action of positive and negative forces in regard to dielectric attractions is similar to one occurring in the preferential condensation of water or alcohol vapor on negatively charged droplets, in comparison with the positively charged droplets in the C. T. R. Wilson cloud method. While there are suggestions to account for the differences in the mobility, such as made by Hassé,[18] who assumes that the negative cluster consists of a group of molecules surrounding an electron, while the positive ion is a similar group of molecules surrounding a positive molecule, these will not suffice. The latter suggestion is particularly unsuccessful as the relation of electrons to molecules assumed is not in accord with modern views as to the relation of the electrons to the molecules, and as it is incapable of accounting for the lower negative mobility in some gases.

To account for these effects one may call upon a limited clustering or a difference in forces of positive and negative ions on molecules. In any case there must be a difference in these forces and one may well inquire into the cause for this, inasmuch as the quantity D as usually used is independent of the sign of the charge.

All forces between ions and molecules and between molecules themselves are largely electrical in nature. Two neutral molecules attract each other according to kinetic theory estimates with forces of the form a/r^5 (the van der Waals forces of cohesion) and repel each other with forces of the form b/r^n, where $n=9$ to $n=11$, which are the repulsive forces defining atomic radii. If one of the attracting molecules is charged the forces are again an attractive one a'/r^5 and a repulsive one $b'/r^{n'}$, which may be different, a' being distinctly larger than a, while b' and n' may be changed in various ways. In one recent theory[11] of ionic mobilities the van der Waals forces have been superposed on the dielectric forces of attraction without any modification. This leads to a prediction of ionic nature and ionic size markedly different from any theory proposed. It is highly questionable whether the two forces may be superposed independently as the van der Waals forces will obviously be altered by the charge on the ion. Were it not for this the theory proposed would have to receive serious consideration.

The outer portions of the molecules are predominatingly negative and for intermolecular distances of the order of a molecular diameter or two, these negative shells are nearer to the positive and negative charges of an ion by an important amount relative to the distances to the positively charged portions of the atoms. The repulsion or attraction of these shells by the positive and negative charges of an ion will not be equal. Hence it is to be expected that a', b' and n' will be different by small amounts for positive and negative ions.

The negative ion will therefore attract most molecules slightly less than the positive ion. Such a difference would account for the fact that the negative ion in general has a higher mobility than the positive ion. This explanation is in essence one first suggested by Yen in a slightly different form.[37] For gases where the positive mobility is greater than the negative mobility, Condon[38] suggests an explanation which may be presented in a slightly more generalized form. In molecules where dipole moments occur which are fairly symmetrically placed relative to the center of the molecules, i.e., relative to the outer shells of electrons, the explanation suggested by Yen should hold and the negative mobility should exceed the positive mobility. For molecules where the dipoles are so placed that the positive constituent is relatively nearer the outer shells of electrons in the molecule, the positive charge will be oriented toward the negative ion and away from the positive ion. The action of this sort will be such as to decrease the effect of the repulsion between the outer shell of the molecule on the negative ion, and where the effect is pronounced it may make the positive mobility greater than the negative mobility. The unsymmetry of the dipole is most pronounced in the case of the halogen acids and here we actually find the greatest decrease of the negative mobility relative to the positive mobility. For other strongly polar compounds like SO_2, H_2O, ROH and H_2S, the effect is present but not in so marked a fashion. The gases which as yet have not been definitely studied in regard to this effect and may invalidate this explanation are the halogens, Cl_2 and Br_2, which are not exceptionally polar. In small concentrations Cl_2 and Br_2 depress the mobility of the negative ions in mixtures well below that of the positive ions. It is however not known whether in pure gases at atmospheric pressure, the positive mobility is greater than the negative mobility or not. Were the former the case the explanation given above would become invalid. Care must, however, be used in these experiments to eliminate HCl, which is usually present with Cl_2 in most methods of preparation, before any conclusions can be drawn.

Conclusions

The explanation given above of the difference in the forces brings still another important feature into the consideration of ionic mobilities. It shows the importance of specific molecular structure in all these considerations. The importance of such structure is also borne out by the effects of traces of

[37] K. L. Yen, Proc. Nat. Acad. Sci. **4**, 106 (1918).

[38] L. B. Loeb, Kinetic Theory of Gases, p. 478.

NH_3, H_2O, ether, Cl_2 and SO_2, which exert very marked specific effects on one ion in a gaseous mixture, leaving the other ion relatively unaffected. All the above facts lead us pretty well to one conclusion, namely, *the mobilities of gaseous ions are controlled as regards order of magnitude and general variation by the dielectric attraction* according to the $(D-1)e^2/2\pi Nr^5$ law, similarly in this respect to the situation in aqueous solutions where it makes little or no difference except in name whether we speak of a cluster or not. In addition there are *secondary effects influencing mobilities, such as changes in concentration of more active molecules about the ion.* These occur and may or may not be of importance. In a sense such effects may as well be described in terms of a statistical clustering effect as in terms of a concentration effect, the terminology having no importance as their action is understood. In part *the above effects may both be influenced by deviations in the intense radial fields surrounding ions,* which cause deviations from the $(D-1)$ law, these deviations depending on the particular electro-chemical structure of the molecules and ions. Finally there is no doubt *that actual clustering of a much more permanent and stable sort* comes into play, which causes abrupt changes in mobility, both in mixtures and on aging. It now appears as if *these effects* (because of their magnitude and nature) *probably involve very few molecules,* possibly only one or two. They are *definitely dependent on the electro-chemical structure of molecules and ions and approach in their stability and nature definite chemical combinations,* possibly somewhat of the type of NH_4^+ ions in solution.

We are thus led to conclude that the problem of gaseous ions is not a simple one fitting one theory or the other exclusively, but that probably all types of action assumed occur under appropriate circumstances for normal gas ions. While the picture so drawn seems to be in the main justified by facts, it is far from completely proven and the purpose of this article has been to sum up the newer facts and to state the problem in its present status, with the hope that the presentation so given will lead to further investigations and thus further clarify the situation.

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THERMAL AGITATION OF ELECTRICITY IN CONDUCTORS

By J. B. Johnson

Abstract

Statistical fluctuation of electric charge exists in all conductors, producing random variation of potential between the ends of the conductor. The effect of these fluctuations has been measured by a vacuum tube amplifier and thermocouple, and can be expressed by the formula $\bar{I}^2=(2kT/\pi)\int_0^\infty R(\omega)|Y(\omega)|^2 d\omega$. I is the observed current in the thermocouple, k is Boltzmann's gas constant, T is the absolute temperature of the conductor, $R(\omega)$ is the *real* component of impedance of the conductor, $Y(\omega)$ is the transfer impedance of the amplifier, and $\omega/2\pi=f$ represents frequency. *The value of Boltzmann's constant* obtained from the measurements lie near the accepted value of this constant. *The technical aspects of the disturbance* are discussed. In an amplifier having a range of 5000 cycles and the input resistance R the power equivalent of the effect is $\bar{V}^2/R=0.8\times10^{-16}$ watt, with corresponding power for other ranges of frequency. The least contribution of *tube noise* is equivalent to that of a resistance $R_e=1.5\times10^5 i_p/\mu$, where i_p is the space current in milliamperes and μ is the effective amplification of the tube.

IN TWO short notes[1] a phenomenon has been described which is the result of spontaneous motion of the electricity in a conducting body. The electric charges in a conductor are found to be in a state of thermal agitation, in thermodynamic equilibrium with the heat motion of the atoms of the conductor. The manifestation of the phenomenon is a fluctuation of potential difference between the terminals of the conductor which can be measured by suitable instruments.

The effect is one of the causes of that disturbance which is called "tube noise" in vacuum tube amplifiers.[2] Indeed, it is often by far the larger part of the "noise" of a good amplifier. When such an amplifier terminates in a telephone receiver, and has a high resistance connected between the grid and filament of the first tube on the input side, the effect is perceived as a steady rustling noise in the receiver, like that produced by the small-shot (Schrot) effect under similar circumstances. The use of a thermocouple or rectifier in place of the telephone receiver allows reasonably accurate measurements to be made on the effective amplitude of the disturbance.

It had been known for some time among amplifier technicians that the "noise" increases as the input resistance is made larger. A closer study of this phenomenon revealed the fact that a part of the noise depends on the resistance alone and not on the vacuum tube to which it is connected. The true nature of the effect being then suspected, the temperature of the re-

[1] Johnson, Nature **119**, p. 50, Jan. 8, 1927; Phys. Rev. **29**, p. 367 (Feb. 1927).

[2] The possibility that under certain conditions the heat motion of electricity could create a measurable disturbance in amplifiers has been recognized on theoretical grounds by W. Schottky (Ann. d. Phys. **57**, 541 (1918)). Schottky considered the special case of a resonant circuit connected to the input of a vacuum tube, and concluded that there the effect would be so small as to be masked by the small-shot effect in the tube.

sistance was varied and the result of that test left little doubt that the thermal agitation of electricity in the resistance element was being observed. Further experiments led to the expression of the effect by a formula which, except for a small difference in the numerical constant, was the same as that later developed by Dr. H. Nyquist[3] on a wholly theoretical basis.

The chief results of the measurements may be summarized as follows. The mean-square potential fluctuation over the conductor is proportional to the electrical resistance and the absolute temperature of the conductor. It is independent of the size, shape or material of the conductor. Its apparent magnitude depends on the electrical characteristics of the measuring system as well as on those of the conductor itself. The quantitative data yield a value for Boltzmann's gas constant which agrees well with that obtained by other methods. It is the purpose of this article to describe in more detail these results and the methods by which they were derived, and to discuss the limit which the phenomenon imposes on amplification by vacuum tubes.

Experimental Method and Apparatus

The significance of the mathematical expression for the effect will be developed with the aid of the generalized circuit diagram of Fig. 1. Z is the conductor under investigation, A the amplifier to which it is connected, J the thermocouple ammeter. The amplifier A is characterized by a complex

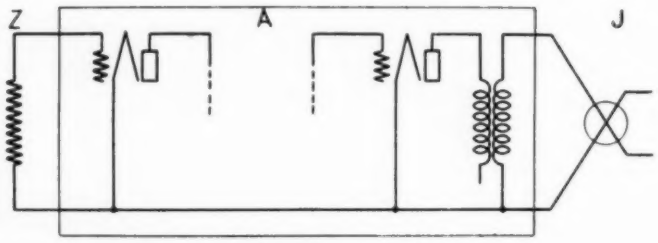

Fig. 1. Simplified diagram of the circuit.

transfer admittance $Y(\omega)$, defined as the ratio of output current to applied input voltage at any frequency $\omega/2\pi=f$. The complex impedance of the element Z has a real resistance component $R(\omega)$ which is also a function of the frequency. The random fluctuation of potential across the input element, arising from the thermal motion of its electric charges, should give rise to a mean-square current $\overline{I^2}$ in the thermocouple according to the equation[4]

$$\overline{I^2}=(2kT/\pi)\int_0^\infty R(\omega)\,|\,Y(\omega)\,|^2 d\omega. \tag{1}$$

T is here the absolute temperature of the input element and k is Boltzmann's gas constant.

[3] Nyquist, Phys. Rev. **29**, 614 (1927); **32**, 110 (1928).
[4] Nyquist, Phys. Rev. **32**, 110 (1928), Eq. (6).

The value of the integral in this expression may be found by graphic integration of the curve formed by the experimentally determined values of $R(\omega)|Y(\omega)|^2$ plotted against ω. In most of the present work the input element Z was a high resistance in parallel with its own shunt capacity and that of its leads and of the input of the amplifier. In such a combination the real resistance component $R(\omega)$ is related to the pure resistance R_0 and the capacity C according to

$$R(\omega) = R_0/(1+\omega^2C^2R_0^2) \tag{2}$$

Two cases now arise. If the input element and the amplifier are so chosen that $R(\omega)$ does not change much over the frequency range of the amplifier, then it is permissible to use the mean value of $R(\omega)$, obtained to a sufficient degree of approximation by replacing ω by ω_0, the frequency of maximum amplification. The factor $R(\omega)$ can then be placed outside the sign of integration and Eq. (1) becomes

$$I^2 = \frac{2kTR_0}{\pi(1+\omega_0^2C^2R_0^2)} \int_0^\infty |Y(\omega)|^2 d\omega. \tag{3}$$

If, on the other hand, $R(\omega)$ cannot be considered constant over the frequency range then the integral must be used as it stands in Eq. (1). The method of determining the various quantities involved in these expressions 1, 2 and 3 will be taken up as the apparatus is described in greater detail.

The amplifier which was used consisted of six stages of audion tubes, suitably coupled, and chosen according to the voltage and power requirements of their various positions. The coupling between tubes was done, with the exception of one interstage, either by transformers or by choke coils and condensers. The exception was a coupling consisting of either a resonant circuit, as shown in Fig. 2, or a band-pass filter, used for the purpose of limiting the amplification to a selected band of frequencies. A comparatively

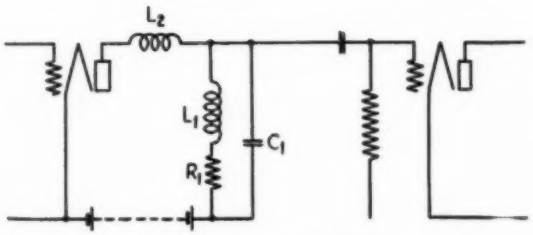

Fig. 2. Diagram of the resonant coupling.

narrow frequency band was admitted by the resonant circuit, the width of the band depending on the relative magnitude chosen for the various components of this system. The band-pass filter, on the other hand, had the frequency range of 500 to 1000 periods per second, with a much sharper cut-off at the limits than the simple resonant circuit.

The amplifier was enclosed in a steel cabinet. It was elaborately shielded against electric, magnetic, acoustic and mechanical shocks, but it was not

always entirely free from these disturbances. Regeneration was apparently negligibly small.

The last tube of the amplifier was coupled by a transformer to a vacuum thermocouple, used with a microammeter as the indicating instrument. The couple was calibrated against a direct current meter of established accuracy. Conveniently, the deflection of the microammeter was closely proportional to the square of the current in the thermocouple.

For the calibration of the amplifier, current sufficiently free from harmonics was obtained from a vacuum tube oscillator. The current was measured by a thermocouple similar to that used in the output. An attenuator of the type described by A. G. Jensen[5] was used so that a known fraction of the current was passed through a resistance of one ohm connected across the input of the amplifier, producing a known input voltage. The corresponding output current was observed. Here, however, a certain correction had

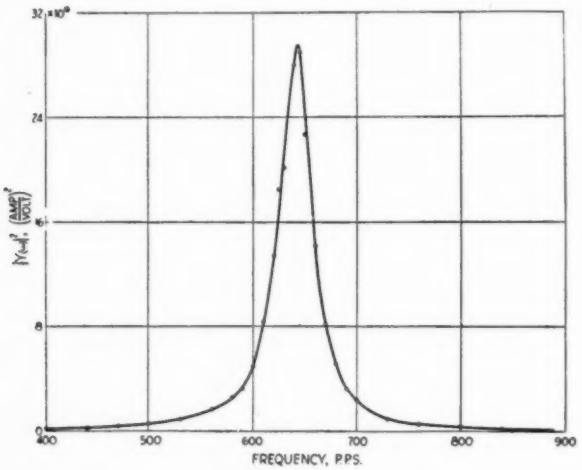

Fig. 3. Typical resonance curve.

to be applied. The amplifier itself, and chiefly the first vacuum tube, produced a disturbance which caused the output meter to deflect even without any external source of input voltage. This "zero deflection" was observed frequently and was subtracted from the total deflection. This could be done, since the mean-square currents added linearly in the deflection, and the value of the mean-square current was desired. The quantity $|Y(\omega)|^2$ was then given by the ratio of the mean-square output current to the mean-square input voltage, which in turn was the ratio of the corrected output deflection to the input deflection, times a multiplier derived from the attenuator setting and the calibrations of the couples. Depending on whether absolute or only comparative measurements were to be made, the determination of $|Y(\omega)|^2$ was done at a series of frequencies or only at the single frequency of maximum amplification. In the latter case the factor $|Y(\omega)|^2$ was only a sort of amplifi-

[5] Jensen, Phys. Rev. **26**, 118 (1925).

cation factor which served as a check on the constancy of the amplifier, while in the former case it was used in the determination of the integral of Eqs. (1) and (3).

A typical curve of amplification factor versus frequency is shown in Fig. 3, obtained from the data for one particular condition of the resonant circuit. The area under curves of this type, establishing the value of the integral, was measured by a planimeter. Since, however, the curves could not be plotted for the full range of the integrals, from zero to infinite frequency, it was necessary to estimate that part of the total area which was limited by the extremes of the characteristic curves. Some of the curves were actually carried out so far (that of Fig. 3, for instance, from 200 to 2200 periods per second) that the further extension to infinite and to zero frequency would have added an almost certainly negligible amount to the total area. Other curves extended only far enough to delimit the greater part of the area, and to the area under these was added a correction arrived at by comparison with the more extensive curves.

An alternating current bridge was used for measuring the resistances R_0 and the capacities C at the frequencies involved. The capacities were of the order 50 mmf. for the input to the amplifier, 10 mmf. for the resistance and from 5 to 150 mmf. for the leads. The effective resistance of the input (grid to filament of the first amplifier tube) was of the order 15 megohms. The measurements of input resistance and capacity were made while the resistance unit was connected in the input of the amplifier, and the amplifier was in the normal operating condition.

Temperature baths were prepared in Dewar flasks when it was desired to keep the resistances at a temperature other than that of the room. The heating or cooling agents were boiling water, melting ice, solid carbon dioxide in acetone, and old liquid air. The temperatures were measured by a platinum resistance thermometer.

There remain to be described the resistance units upon which the experiments were done. These were chosen so as to include materials of different properties, such as high or low resistivity, positive or negative temperature coefficient, metallic or electrolytic conduction, light ions or heavy ions. In value the resistances ranged from a few thousand ohms to a few megohms.

For values of more than one-half megohm commercial "grid leak" resistances were used, made with India ink on paper. Another type of commercial product, made of carbon filament wound on lavite, covered the range of resistance below one megohm. Platinum and copper resistances were used in the form of thin films deposited on glass by evaporation. A resistance of nearly a half megohm was made of Advance wire, wound non-inductively. This was provided with a tap so that one-third or two-thirds of it could be used.

Electrolytic resistances were made of aqueous solutions of the salts NaCl, $CuSO_4$, K_2CrO_4, $Ca(NO_3)_2$, and of a solution of sulphuric acid in ethyl alcohol. Glass tubes about 15 cm long, some of capillary size and some larger, were filled with the different solutions of such strength as to give them

all about the same resistance, and this was repeated with another resistance value.

Measurements and Results

A considerable part of the work consisted of comparative measurements in which the characteristics of the amplifier did not need to be known. In these circumstances only the maximum amplification was determined. It was convenient in such cases to think of the resistance as impressing on the amplifier a mean-square potential $\overline{V}^2$. By this method of comparison was determined the fact that the phenomenon is independent of the material and shape of the resistance unit and of the mechanism of the conduction,[6] but does depend on the electrical resistance. A few of the results are reproduced in Fig. 4. They are expressed in terms of $\overline{V}^2$, the apparent mean-square potential fluctuation, plotted against the resistance component $R(\omega)$. The points lie close to a straight line. The quantity $W=\overline{V}^2/R(\omega)$, which may be

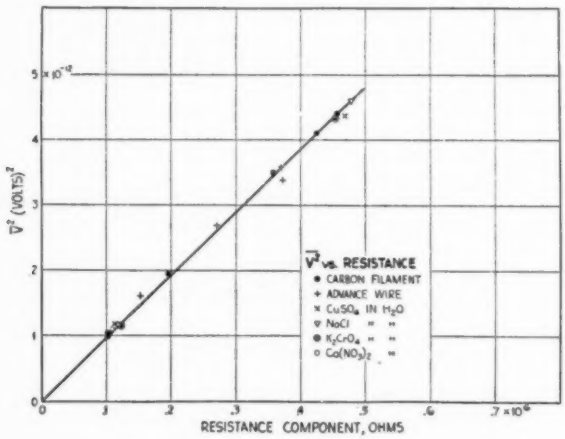

Fig. 4. Voltage-squared vs. resistance component for various kinds of conductors.

called the power equivalent of the effect, is independent of all the variables so far considered, including the electrical resistance itself.

The effect of the shunt capacity C across the conductor is shown in Fig. 5. In this case the abscissae are the measured values of resistance R_0, the circles marking the observed values of the apparent $\overline{V}^2$. These values of $\overline{V}^2$ reach a maximum and then actually decrease as the resistance is indefinitely increased. Obtaining a factor of proportionality K from the initial slope of the curve and using the measured value of C and ω for the calculation of $\overline{V}^2=KR(\omega)=KR_0/(1+\omega^2C^2R_0^2)$, the expected values of $\overline{V}^2$ were calculated. These are represented by the curve in Fig. 5. The course of the calculated curve agrees well with that for the observed points. The agreement was also verified by using a fixed resistance and adding known shunt capacities up to as high as 60,000 mmf.

[6] Resistances such as thermionic tubes and photoelectric cells, perhaps all resistances not obeying Ohm's law, are exceptions to this rule. In these the statistical conditions are different.

The effect of the temperature of the resistance element was studied chiefly by the same comparative method that was used for the varied resistances. The experiments were done on the Advance wire resistance and on carbon filament resistances over the temperature range from −180°C (liquid air) to 100°C (boiling water). They were also done on two liquid resistances made of alcohol and sulphuric acid, covering a range of tempera-

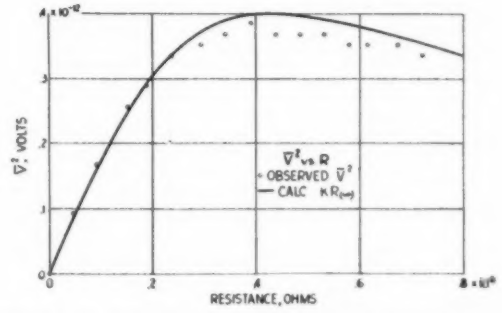

Fig. 5. Voltage-squared vs. resistance with fixed shunt capacity; frequency 635 p.p.s., capacity 577 mmf.

tures from −72°C to 90°C. The resistance values used in the computations were those measured at the various temperatures. Advance wire and carbon filaments changed very little in resistance over the temperature range used for them, while that of the liquid elements changed tremendously, increasing for lower temperatures. In all cases, however, the virtual power $\overline{V}^2/R(\omega)$

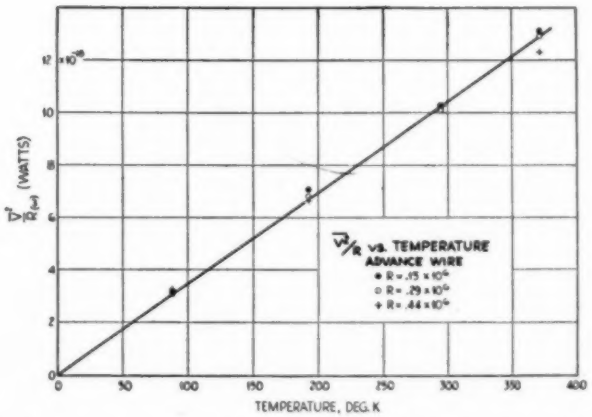

Fig. 6. Apparent power vs. temperature, for Advance wire resistances.

was proportional to the absolute temperature of the resistance element. Fig. 6 shows graphically the results for the three Advance wire resistances. The other resistances gave values falling closely on the same straight line as these.

There is finally to be recounted the verification of Eqs. (1) and (3) as they involve the electrical properties of the measuring system. The method

of obtaining the frequency characteristic of the amplifier, the graphic integration of this curve and the corrections that were applied, have already been described. For these determinations the amplifier was altered in various ways, but usually by changing the resonant circuit forming one of the interstage couplings, or by replacing this circuit by the band-pass filter. The natural frequency of the resonant circuit was changed, by means of the inductance or condenser, over the range of 300 to 2000 periods per second. The sharpness of resonance was varied by changing either the resistance in the resonant circuit or the inductance in series with this circuit and the tube. The area under the characteristic curve could thus be made larger or smaller over a considerable range.

The input resistance element, in all of this work, was kept at only slightly above room temperature. It was of the "grid leak" type for most of those measurements in which the resonant circuit was employed, while the Advance

TABLE I. *Determination of Boltzmann's Constant.*

No.	f	T	$R(\omega)$	$\int_0^\infty \lvert Y(\omega)\rvert^2 d\omega$	$\int_0^\infty \lvert Y(\omega)\rvert^2 R(\omega) d\omega$	ΔS	$\overline{I^2}$	k
	p.p.s.	°K	$\times 10^{-6}$	$\times 10^{-10}$	$\times 10^{-16}$	%	$\times 10^{6}$	$\times 10^{16}$
1	1010	298	.526	.213		12.0	2.7	1.27
2	2023	"	.470	.272		26.2	2.8	1.15
3	1418	"	.508	.361		15.6	3.8	1.09
4	"	"	"	.188		42.3	1.8	.99
5	295	"	.548	.252		3.3	3.1	1.18
6	"	"	"	.202		15.8	2.0	.95
7	302	"	"	.221		12.4	2.7	1.18
8	"	"	"	.195		15.3	2.3	1.13
9	653	"	.541	.747		6.8	10.4	1.14
10	"	"	"	.645		12.9	8.6	1.30
11	1418	"	.508	.286		18.5	3.5	1.26
12	"	"	"	.161		41.3	1.7	1.09
13	1465	"	.505	1.93		18.7	21.2	1.14
14	"	"	"	1.75		20.3	19.1	1.14
15	635	"	.541	.594		8.8	8.9	1.46
16	"	"	"	.139		35.0	2.1	1.47
17	"	"	"	.597		10.9	7.8	1.28
18*	643	295	.44 ±		.439	0	11.0	1.38
19	645	297	"		.396	0	11.1	1.49
20	1830	301	"		.913	0	19.8	1.13
21	500–1000	299	"		.831	0	25.9	1.64
22	"	300	"		.662	0	21.5	1.70
23	"	300	"		.832	0	26.0	1.63

* The resonance curve for this determination is that reproduced in Fig. 3.

wire resistance was used as input element in connection with the band-pass filter. The resistance and capacity of each was measured accurately *in situ*, the resistance being of the order of one-half megohm.

The results will be presented in terms of the value of Boltzmann's constant k, as calculated from the data according to Eqs. (1) or (3). The last column of Table I contains these calculated values, while in the other columns of the table are indicated some of the experimental conditions involved in each determination. The columns of the table indicate, in order,

the resonance frequency or frequency range of the selective circuit, the temperature and the ohmic value of the input resistance component, and the value of one or the other infinite integral. The column under ΔS contains the part, in percent, which the estimated area contributes to the total integral. $\bar{I}^2$ is the current-squared observed in the thermocouple.

The average of the values of k in the last column of the table is 1.27×10^{-16} ergs per degree, with a mean deviation of 13 percent. The average is 7.5 percent lower than the accepted value[7] of k, 1.372×10^{-16} ergs per degree. The series of measurements, therefore, yields a value of k which is correct within the mean deviation. I believe, however, that the method is capable of a much higher accuracy than that obtained here. This leads to a discussion of the possible sources of error.

An inspection of the tabulated data reveals no systematic relation of the value of k to the numbers in any one column, except that the results of the last three measurements, made with the band-pass filter, are higher than the rest. The deviations are apparently distributed at random. Among the quantities which enter Eq. (1) there can be little question of the accuracy of the temperature T and the resistance component $R(\omega)$. The error is therefore to be sought in the current-squared, $\bar{I}^2$, and in the integral of $|Y(\omega)|^2 d\omega$. The latter is indeed open to the criticism that the correction term for the area was often large and therefore uncertain, but this cannot be held against the last six determinations. It is possible, because of feedback through the internal capacities of the tubes, that the amplification of the system was not the same when the resistance alone was connected across the input as when this was shunted by the low resistance of the calibration circuit. It is not clear, however, how such a change in amplification could make the values of k sometimes too large and at other times too small. The other debatable factor, $\bar{I}^2$, may be questioned in two respects. There was a "zero reading," due to tube noise, amounting usually to about ten percent of the total reading of the meter used for measuring $\bar{I}^2$. This zero reading, however, was always quite constant. The total reading, on the other hand, was not constant but fluctuated over a range comprising about five percent of the total reading. This unsteadiness might be caused by disturbances generated either within the amplifier or coming from the outside, or it might represent a natural fluctuation in the phenomenon itself. Two different procedures were used in obtaining the reading. At first a single datum was used, taken after watching the needle for perhaps thirty seconds. Judgment placed this value nearer the lower limit of the excursion of the needle, since disturbances would tend to make the readings high. For each of the last six sets of measurements, Nos. 18 to 23, the average of a series of readings was used. The meter was read at about one hundred equally spaced intervals of time, before and after obtaining the frequency characteristic of the system. The average of these readings was slightly greater than that arrived at by judging the undisturbed position of the needle.

[7] Int. Crit. Tables, v. 1, p. 18.

Whatever the cause of the deviation, the fact remains that there is essential agreement in all respects between the theory and the experimental results. It is remarkable that the same apparatus by which it is possible to determine the charge on the electron by means of the small-shot effect, can by a slight change in procedure be made to yield an independent measurement of Boltzmann's gas constant.

Technical Aspects of the Phenomenon

Since the thermal agitation places a limit on what can be done by amplifiers, it will be of interest to discuss this limit in terms more commonly used than those of Eq. (1). It is more convenient to speak of a disturbance to an amplifier as a voltage fluctuation at the input than as a current fluctuation at the output which has been used here. A voltage fluctuation across the input of the amplifier cannot, in general, logically be derived from Eq. (1). Certain simplifying conditions may be assumed, however, which make such a derivation plausible. Let us take a circuit having constant amplification over the frequency range f_1 to f_2, zero amplification outside this range. The input resistance component may be assumed to have the constant value R within the frequency range of the circuit. Eq. (1) may then be written

$$\overline{I^2}=(2kTRY^2/\pi)(\omega_2-\omega_1)=4kTRY^2(f_2-f_1)=4kTR(f_2-f_1)\overline{I^2}/V^2, \qquad (4)$$

where V is the r.m.s. voltage, having any frequency within the pertinent range, applied at the input of the amplifier, and I is the current produced at the output of the circuit. Now the voltage V may be given such a magnitude that the corresponding output current-squared equals that produced by the thermal agitation in the resistance R. The value of V^2 can then be considered equivalent to the voltage-squared generated by the thermal agitation and may be denoted by $\overline{V^2}$. Eq. (4) becomes

$$\overline{I^2}=4kTR(f_2-f_1)\overline{I^2}/\overline{V^2}\,;$$

$$\overline{V^2}=4kTR(f_2-f_1)=WR\,; \qquad (5)$$

$$W=\overline{V^2}/R=4kT(f_2-f_1)\,. \qquad (6)$$

W is the virtual power, which in its effect on the output meter is equivalent to an actual power of this value dissipated in the input resistance. For an amplifier operated at room temperature and covering the approximate voice frequency range of 5000 cycles this power is

$$W=4\times 1.37\times 10^{-16}\times 300\times 5000\times 10^{-7}=0.82\times 10^{-16}\text{ watt}.^{8}$$

If the input resistance is one-half megohm the mean-square voltage fluctuation is $\overline{V^2}=WR=0.82\times 10^{-16}\times 0.5\times 10^{6}=0.41\times 10^{-10}$ (volts)^2, to which corresponds an apparent input voltage of 6.4 microvolts. A value very close

[8] The value of 10^{-15} watt given in the cited notes was for the narrower frequency band of a resonant circuit.

to this was actually observed when the experimental amplifier was given approximately the characteristics assumed here.

For input elements other than pure resistance the problem cannot be handled in this simple way, but Eq. (1) should still apply as it has been seen to do in the case of the resistance-capacity combination. When a resonant circuit was used in the input, however, the observed value of I^2 was somewhat greater than that computed from the characteristics of the system. The difficulty was, no doubt, that it was impossible by means conveniently at hand to shield the inductance coil well enough against magnetic disturbances of external origin.

Towards the problem of reducing the noise in amplifiers caused by thermal agitation the theory makes three suggestions. The first is the use of a low input resistance. This factor, however, is not usually entirely at our disposal, being influenced by the apparatus which supplies the small voltage that is to be amplified. Secondly, the input resistance may be kept at a low temperature. This expedient, too, has practical limitations since the elements which make up the input resistance cannot always conveniently be confined in a small space. The third possible way to reduce the noise consists in making the frequency range of the system no greater than is essential for the proper transmission of the applied input voltage.[9] For the purpose of detecting or measuring a voltage of constant frequency and amplitude one may go to extremes in making the system selective and thereby proportionately reducing the noise. One may, for instance, make use of the great sharpness of tuning obtained by means of mechanical rather than electrical resonance. When, however, the applied voltage varies in frequency or amplitude, the system must have a frequency range large enough to take care of these variations, and the presence of a certain level of noise must be accepted. Beyond this, the chief value of the knowledge gained here lies in the ability it gives to predict the lower limit of noise in any case, so that the impossible will not be expected of an amplifier system.

The noise of thermal agitation is usually the predominant source of disturbance in a well constructed amplifier. Thermionic tubes, however, produce a noise of the same nature, which may exceed the thermal noise when the input resistance component is small. This tube noise is a result of fluctuations in the space current of the tube.[10] When tubes are operated at too low a filament temperature the greater part of these fluctuations are caused by the phenomena named by Schottky "small-shot effect" and "flicker effect." In tubes operated with full space charge limitation of the current, the small-shot effect and flicker effect are largely or perhaps entirely suppressed by the space charge. Under these conditions, and with the grid connected directly to the filament, there is still a remanent fluctuation of current in the tube. In a rough way the amount of this disturbance may be de-

[9] The principle holds for disturbances of other kinds, cf. J. R. Carson, Bell System Tech. J. 4, 265 (1925).

[10] Johnson, Phys. Rev. 26, 71 (1925); A. W. Hull, Phys. Rev. 25, 147 (1925); Phys. Rev. 27, 439 (1926); W. Schottky, Phys. [illegible] 74 (1926).

scribed in terms of the resistance R_c which when connected between the grid and filament of the tube would cause an equal disturbance in the amplifier, so that the total noise is given by the relation

$$\overline{V^2} = W(R+R_c). \tag{7}$$

The order of magnitude of this resistance R_c, for a tube connected for operation in the range of voice frequencies, may be estimated from the working formula

$$R_c = 1.5\times 10^3 i_p/\mu^2, \tag{8}$$

the symbol μ standing for the effective amplification of the tube in combination with its external output impedance, i_p for the space current in the tube measured in milliamperes. Consider, as an example of this rule, a tube having a space current $i_p = 0.5$ milliampere and an amplification factor $\mu_0 = 30$, working into an external impedance equal to its own internal plate resistance. The effective amplification is then $\mu = 15$, and the minimum noise of the tube should be equal to that of a resistance $R_c = 5{,}000$ ohms in the grid circuit of the tube. If the tube works into an amplifier such as was previously considered this tube noise is therefore equivalent to an effective voltage of .9 microvolt impressed on the grid of the tube. It is not suggested that the predicted minimum noise can be attained with every tube. Many tubes, defective in some way or other, have noise levels much higher than the minimum. It is seen, however, that with the best tubes, properly operated, the tube noise is important only when the resistance component of the input circuit is smaller than the equivalent resistance R_c. With resistances greater than this the thermal agitation should contribute the preponderant part of the noise.[11]

It is interesting to note that in another field of measurements the effect of the thermal agitation of charge in conductors has made itself felt. A group of workers[12] in the Netherlands observed that the deflection of a highly sensitive string galvanometer executed random deviations from the zero position. They ascribed this phenomenon, evidently correctly, in part to "Brownian motion of current" in the galvanometer system. Since then the phenomenon has been further investigated,[13] both theoretically and experimentally, with the conclusion that with a galvanometer the measurement of

[11] In my earlier paper (l.c. 10) the relation of noise to amplification for a number of tubes is shown in Fig. 13. When these data were obtained *a resistance of one-half megohm was connected between the grid and filament of the tube*, a connection which was thought more normal than having no resistance in the grid circuit. The lower limit of noise appears therefore to have been "resistance noise" rather than "tube noise" as this term is now used. Since the noise was measured at the output of the amplifier it is natural that the observed noise should have increased with increasing amplification constant of the experimental tube.

[12] W. Einthoven, F. W. Einthoven, W. van der Hoist & H. Hirschfeld, Physica **5**, 358 (1925).

[13] J. Tinbergen, Physica **5**, 361 (1925); G. [illegible] Phil. Mag. **1**, 827 (1926); F. Zernike, Zeits. f. Physik **40**, 628 (1926); A. V. Hill, J. Sc. Instr. **4**, 72 (1926).

direct current of less than 10^{-12} ampere becomes unreliable, just as the alternating potential of 10^{-6} volt marks a critical region for amplifiers.

In conclusion, I wish to acknowledge my indebtedness to Dr. O. E. Buckley for the helpful criticism he has given during the course of this work; and to Mr. J. H. Rohrbaugh for assistance in the measurements.

BELL TELEPHONE LABORATORIES, INCORPORATED,
December 20, 1927.*

* Received April 19, 1928. Ed.

THERMAL AGITATION OF ELECTRIC CHARGE IN CONDUCTORS*

By H. Nyquist

Abstract

The electromotive force due to thermal agitation in conductors is calculated by means of principles in thermodynamics and statistical mechanics. The results obtained agree with results obtained experimentally.

DR. J. B. JOHNSON[1] has reported the discovery and measurement of an electromotive force in conductors which is related in a simple manner to the temperature of the conductor and which is attributed by him to the thermal agitation of the carriers of electricity in the conductors. The work to be resported in the present paper was undertaken after Johnson's results were available to the writer and consists of a theoretical deduction of the electromotive force in question from thermodynamics and statistical mechanics.[2]

Consider two conductors each of resistance R and of the same uniform temperature T connected in the manner indicated in Fig. 1. The electromotive force due to thermal agitation in conductor I causes a current to be set up in the circuit whose value is obtained by dividing the electromotive force by $2R$. This current causes a heating or absorption of power in conductor II, the absorbed power being equal to the product of R and the square of the current. In other words power is transferred from conductor I to conductor II. In precisely the same manner it can be deduced that power is transferred from conductor II to conductor I. Now since the two conductors are at the same temperature it follows directly from the second law of thermodynamics that the power flowing in one direction is exactly equal to that flowing in the other direction. It will be noted that no assumption has been made as to the nature of the two conductors. One may be made of silver and the other of lead, or one may be metallic and the other electrolytic, etc.

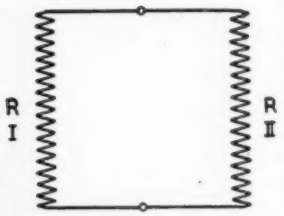

Fig. 1.

It can be shown that this equilibrium condition holds not only for the total power exchanged by the conductors under the conditions assumed, but also for the power exchanged within any frequency. For, assume that this is not so and let A denote a frequency range in which conductor I delivers more power than it receives. Connect a non-dissipative network between the two conductors so designed as to interfere more with the transfer of energy

* A preliminary report of this work was presented before the Physical Society in February, 1927.

[1] See preceding paper.

[2] Cf. W. Schottky, Ann. d. Physik 57, 541 (1918).

in range A than in any other range, for example, a resonant circuit connected as indicated in Fig. 2 and resonant within the range A. Since there is equilibrium between the amounts of power transferred in the two directions before inserting the network, it follows that after the network is inserted more power would be transferred from conductor II to the conductor I than in the opposite direction. But since the conductors are at the same temperature, this would violate the second law of thermodynamics. We arrive, therefore, at the important conclusion that the electromotive force due to thermal agitation in conductors is a universal function of frequency, resistance and temperature and of these variables only.[3]

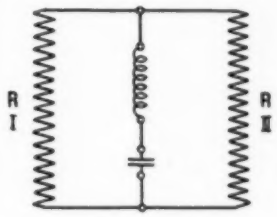

Fig. 2.

To determine the form of this function consider again two conductors each of resistance R connected as shown in Fig. 3 by means of a long non-dissipative transmission line, having an inductance L and a capacity C per unit length so chosen that $(L/C)^{1/2}=R$. In order to avoid radiation one conductor may be internal to the other. Under these conditions the lines has the characteristic impedance R, that is to say the impedance of any length of line when terminated at the far end in the impedance R presents the impedance R at the near end and consequently there is no reflection at either end of the line. Let the length of the line be l and the velocity of propagation

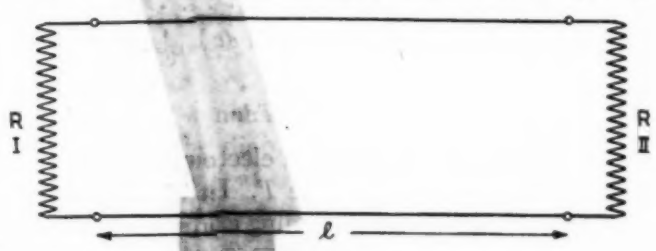

Fig. 3.

v. After thermal equilibrium has been established, let the absolute temperature of the system be T. There are then two trains of energy traversing the transmission line, one from left to right in the figure, being the power delivered by conductor I and absorbed by the conductor II, and another train in the reverse direction.

At any instant after equilibrium has been established, let the line be isolated from the conductors, say, by the application of short circuits at the two ends. Under these conditions there is complete reflection at the two ends and the energy which was on the line at the time of isolation remains trapped. Now, instead of describing the waves on the line as two trains traveling in opposite directions, it is permissible to describe the line as vibrating at its natural frequencies. Corresponding to the lowest frequency

[3] For a general treatment of the principle underlying the discussion of this paragraph reference is made to P. W. Bridgman, Phys. Rev. 31, 101 (1928).

the voltage wave has a node at each end and no intermediate nodes. The frequency corresponding to this mode of vibration is $v/2l$. The next higher natural frequency is $2v/2l$. For this mode of vibration there is a node at each end and one in the middle. Similarly, there are natural frequencies $3v/2l$, $4v/2l$, etc. Consider a frequency range extending from ν cycles per second to $\nu+d\nu$ cycles per second, i.e., a frequency range of width $d\nu$. The number of modes of vibration, or degrees of freedom, lying within this range may be taken to be $2ld\nu/v$, provided l is taken sufficiently large to make this expression a great number. Under this condition it is permissible to speak of the average energy per degree of freedom as a definite quantity. To each degree of freedom there corresponds an energy equal to kT on the average, on the basis of the equipartition law, where k is the Boltzmann constant. Of this energy, one-half is magnetic and one-half is electric. The total energy of the vibrations within the frequency interval $d\nu$ is then seen to be $2lkTd\nu/v$. But since there is no reflection this is the energy within that frequency interval which was transferred from the two conductors to the line during the time of transit l/v. The average power, transferred from each conductor to the line within the frequency interval $d\nu$ during the time interval l/v is therefore $kTd\nu$.

It was pointed out above that the current in the circuit of Fig. 1 due to the electromotive force of either conductor is obtained by dividing the electromotive force by $2R$, and that the power transferred to the other conductor is obtained by multiplying the square of the current by R. If the square of the voltage within the interval $d\nu$ be denoted by $E^2d\nu$ we have, therefore

$$E^2d\nu = 4RkTd\nu \tag{1}$$

This is the expression for the thermal electromotive force in a conductor of pure resistance R and of temperature T. Let it next be required to find the corresponding expression for any network built up of impedance members of the common temperature T. Let the resistance R be connected, as shown in Fig. 4, to any such network having the impedance $R_\nu+iX_\nu$, where R_ν and X_ν may be any function of frequency. By reasoning entirely similar to that used above it is deduced that the power transferred from the conductor to the impedance network is equal to that transferred in the opposite direction. But the former is shown by simple circuit theory to be equal to

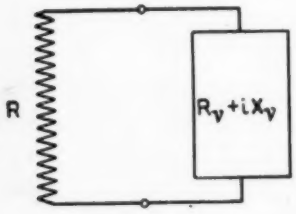

Fig. 4.

$$E^2R_\nu d\nu/[(R+R_\nu)^2+X_\nu] \tag{2}$$

and the latter is similarly equal to

$$E_\nu^2Rd\nu/[(R+R_\nu)^2+X_\nu] \tag{3}$$

where $E_\nu^2d\nu$ is the square of the voltage within the frequency range $d\nu$. It follows that

$$E_\nu^2 d\nu = 4R_\nu kT d\nu \tag{4}$$

for any network.

To put this relation in a form suitable for comparison with measurements let $Y(\omega)$ be the transfer admittance of any network from the member in which the electromotive force in question originates to a member in which the resulting current is measured. Let $\omega = 2\pi\nu$ and let $R(\omega) = R_\nu$ be the resistance of the member in which the electromotive force is generated. We have then for the square of the measured current within the interval $d\nu$

$$I^2 d\nu = E_\nu^2 \mid Y(\omega) \mid^2 d\nu = (2/\pi) kT R(\omega) \mid Y(\omega) \mid^2 d\omega \tag{5}$$

Integrating from 0 to ∞

$$I^2 = (2/\pi) kT \int_0^\infty R(\omega) \mid Y(\omega) \mid^2 d\omega \tag{6}$$

which is Eq. (1) in Johnson's paper.

It will be noted that such quantities as charge, number, and mass of the carriers of electricity do not appear explicitly in the formula for electromotive force These quantities influence R_ν, however, and, therefore, enter indirectly.

It is instructive to consider the equilibrium between the thermal agitation of the carriers of electricity in a conductor and the thermal agitation of molecules in a gas. Consider a semi-infinite tube filled with gas of temperature T and let the end be closed in a weightless inflexible piston forming the diaphragm of an ideal non-dissipative telephone receiver having no magnetic leakage. Such a receiver presents an electrical impedance which is a function of the mechanical impedance of the gas in the tube and which may be taken as R by choosing a suitable number of turns for the receiver element. Due to the bombardment of the diaphragm by the molecules in the gas, there will be an electromotive force at the terminals of the receiver. This electromotive force is, of course, in statistical equilibrium with that due to thermal agitation in a conductor of resistance R. It follows that it should be possible to calculate that electromotive force from the kinetic theory of gases, but this calculation would not be so direct as that given above, making use of a transmission line.

In what precedes the equipartition law has been assumed, assigning a total energy per degree of freedom of kT. If the energy per degree of freedom be taken

$$h\nu/(e^{h\nu/kT} - 1) \tag{7}$$

where h is the Planck constant, the expression for the electromotive force in the interval $d\nu$ becomes

$$E_\nu^2 d\nu = 4R_\nu h d\nu/(e^{h\nu/kT} - 1). \tag{8}$$

Within the ranges of frequency and temperature where experimental information is available this expression is indistinguishable from that obtained from the equipartition law.

AMERICAN TELEPHONE AND TELEGRAPH COMPANY,
April, 1928.

EVIDENCE OBTAINED BY X-RAY ANALYSIS OF FILMS OF IRON IN MAGNETIC FIELDS AS TO THE ULTIMATE NATURE OF MAGNETISM

By T. D. Yensen

Abstract

The results of K. T. Compton and Trousdale (1915) and of A. H. Compton and Rognley (1918 and 1920) showed that there is no change in the crystal structure of single crystals of magnetite and hematite when placed in strong magnetic fields. In the present investigation films of electrolytic iron were analyzed by x-rays to determine whether there is any change in the random orientation of the minute crystals (of the order of 150A) found in these films when placed in strong magnetic fields (up to 2600 gausses). If so, the uniform circular diffraction patterns resulting from the randomly oriented crystals should, because of the preferred orientation, be changed to show greater or less density along a diameter parallel to the applied magnetic force than along the other, perpendicular to it. The circles were analyzed micro-photometrically and the results indicate no change in the orientation. The average of all the measurements is a ratio of the intensities along the two diameters of 1.00 ± 0.08, the variation being attributed to incidental sources arising from the developing and handling of the film. The conclusion, therefore, is that the most minute crystal aggregates in iron are not oriented in a magnetic field and lends strength to the previous conclusion in regard to the ultimate nature of magnetism, namely, that the magneton is an atomic property.

1. Introduction

THE discovery of the electron and the advances in our knowledge of the atomic structures—based largely on close agreement between Bohr's theory and the accumulated data on spectral lines—makes it reasonable to assume that the atom consists of electrons moving in orbits about a central nucleus and consequently equivalent to a "magnetic particle." The Amperian hypothesis is thus rapidly becoming a reality and we are slowly beginning to regard magnetism purely and simply as the evidence of electricity in motion and the magneton as an atomic property, the external manifestation of the motion of electrons. This view is further confirmed by the experiments of Richardson,[1] Einstein and de Haas[2] and by Barnett[3] on magnetization by rotation, and vice versa, and also by that of Joffe[4] in which he obtained a definite rotational kick in a suspended magnetized nickel bar, when heated to the Curie point. All these experiments show definitely that the magneton acts like a spinning top. The fact that the numerical values obtained for the magneton in these cases is very nearly double that of the

[1] O. W. Richardson, Phys. Rev. **26**, Ser. I, 248 (1908).

[2] Einstein and de Haas, Verb. d. D. G. **17**, 152, 420 (1915); Einstein, Verb. d. D. G. **18**, 173 (1916); de Haas, Verb. d. D. G. **18**, 423 (1916); de Haas, Proc. Am. Acad. **18**, 1281 (1916).

[3] Barnett, S. J. Bull. Nat. Research Council **3**, 235 (1922).

[4] Oral information by Dr. Joffe to the writer during the former's visit to California Institute of Technology in 1927.

Bohr magneton, calculated on the basis of an electron in the normal hydrogen orbit

$$\mu_B = eh/4\pi m$$

may necessitate the introduction of the spinning electron, but this is of minor importance. The main point is that it may be possible to identify the magneton with a rotating or a spinning electron.

From x-ray data on single magnetite and hematite crystals obtained with a field intensity of 1000 gausses, K. T. Compton and Trousdale[5] in 1915 found no change in the x-ray pattern with and without fields. They concluded therefore that there is no relative translation of the atoms on magnetization, and that the ultimate magnetic particle is the atom or something within the atom. Later, 1918–20, A. H. Compton and Rognley[6] repeated the experiment with magnetite but went a step further, in that they measured the intensity of the reflected x-ray beam by means of an electroscope with the crystal in the neutral and in the magnetized (1/3 saturated) state. The change in intensity was less than 1 percent. Based on the theory that the reflected intensity in any one direction is a function of the arrangement of the atoms in the crystal and also of the arrangement of the electrons in the atom, these investigators concluded that the ultimate magnetic particle cannot be a group of atoms, as a change in their mutual discance of 1/300 part would have been detected.They went even so far as to]onclude that the ultimate magnetic particle cannot be the atom as a whole, ᵇs a change in orientation of the atom as a whole would have been detected by their experiments. The only units that remained capable of orientation were the nucleus and the individual electrons, and they concluded from auxiliary evidence that it is most probable that the ultimate magnetic particle is the spinning electron.

These conclusions, however, do not preclude the possibility that in metallic substances like iron, there may be minute crystal aggregates whose orientation is affected by the magnetic field and which consequently may cause dissipation of energy and otherwise influence the magnetic properties.

The present investigation was undertaken with the object of ascertaining whether there are present in iron samples minute cyrstals of any kind that assume a preferred orientation when the sample is placed in a magnetic field.

Based on the results obtained, the answer must be a negative one. Even with the minutest crystals of submicroscopic dimensions, such as exist between the main crystals in iron, the evidence indicates no change in the random orientation, even when a magnetic force sufficient to produce magnetic saturation is applied. The results therefore incidentally confirm the hypothesis that the ultimate magnetic particle is an intra-atomic unit.

[5] K. T. Compton and E. A. Trousdale, Phys. Rev. **5**, Ser. II, 315 (1915).

[6] A. H. Compton and O. Rognley, Phys. Rev. **11**, Ser. II, 132 (1918); **16**, Ser. II, 464 (1920).

2. Hysteresis Loss in the Intercrystalline Material

That the hysteresis loss in iron depends to some extent on the intercrystalline material has been known for some time. It was noticed qualitatively by Ruder[7] in testing silicon steel and later by the writer[8] in investigating the magnetic properties of pure iron and iron-silicon alloys. The data obtained by the writer indicated a relation between N, the number of grains or crystal aggregates per mm^2 (used as a measure of the amount of intercrystalline material) and the hysteresis loss W_h (in ergs per cm^3 per cycle for $B = 10{,}000$ gausses) that could be expressed by the empirical equation

$$W_h = 65N^{1/2}$$

Last year Honda[9] came to a similar conclusion, the only difference being in the form of the function.

Based on the hypothesis that hysteresis in ferromagnetic metals may be due to the orientation and reversal in the magnetic field of the minute crystals making up the intercrystalline material, it was suggested by Dr. P. S. Epstein that this idea might be tested by passing a beam of homogeneous x-rays through a thin strip of iron, so treated as to provide a large amount of intercrystalline material. The minute crystals, if randomly oriented would produce uniform circles on the photographic film. If the minute crystals are oriented more or less when the sample is placed in the magnetic field the circles, instead of being uniformly dense, would be denser along one diameter than along another at right angles to it.

In the preliminary experiment, to try out the suggestion, samples of ingot iron were used, prepared at the Westinghouse Research Laboratory according to the writer's specifications. All samples consisted of 0.356 mm (0.014″) thick discs 4.45 cm (1.75″) in diameter. They were all annealed at 950°C for one hour in vacuum in order to eliminate rolling effects, and were then treated as follows:

Samples A—cooled with the furnace; B—cooled 30° per hour to 600° and then with the furnace; C—removed from the furnace at 950° and cooled in air; D—removed from the furnace at 950° and quenched in water. The reason for these heat treatments, aside from elimination of rolling effects, is that pure iron recrystalizes at 900°C. By cooling at various rates through this point it is possible to obtain a variation in grain size, the smallest grains being obtained when the iron is quenched in air (C), or in water (D).

3. The First X-Ray Analyzing Apparatus

The general arrangements of the first apparatus is shown in Fig. 1. The current for the x-ray tube was obtained from a 5 KVA, 60 cycle, 110 to 100,000 volt transformer with the middle point grounded. Each side of the

[7] Ruder, Bull. A.I.M.E. No. 84, p. 2805 (1913).

[8] Yensen, Trans. A.I.E.E. **43**, 145 (1924).

[9] Honda, Nature **117**, 753–54 (1926). No reference is made by Honda to the previous results obtained by Ruder and by the writer.

high voltage winding was connected to a kenotron tube so that both half waves were utilized. A Coolidge molybdenum-target x-ray tube was used, requiring for the excitation of the K_α line about 20,000 volts. The voltage actually used was 35,000, with a cathode current of about 27 ma. The distance from the cathode to the fixed pinhole was about 15 cm; that between the 2 pinholes about 5 cm; from the adjustable pinhole to the sample about 2.5 cm; and from the sample to the film 13.1 cm. The pinholes (in lead) were approximately 0.5 mm in diameter. Between the adjustable pinhole and the sample was provided a lead disc with a hole about 2.5 mm in diameter to cut out all scattered x-ray radiation from the edge of the adjustable pinhole,

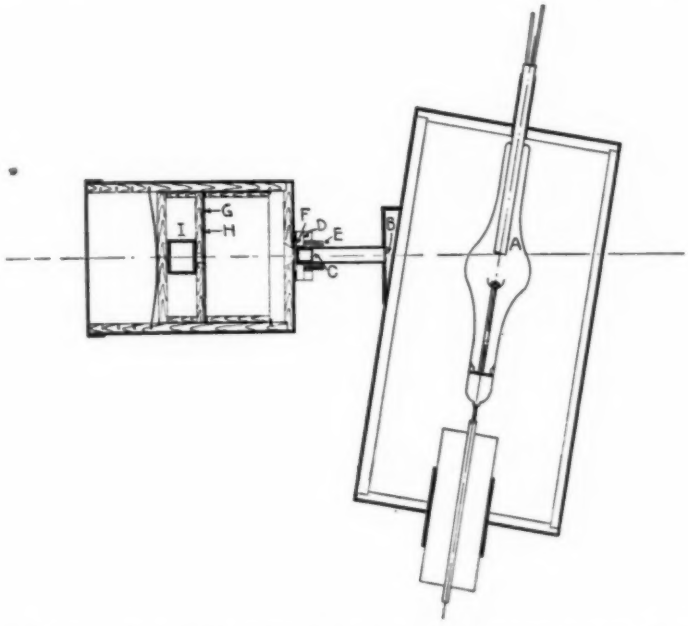

Fig. 1. X-ray analyzing apparatus No. 1. A, molybdenum target; B, fixed pinhole; C, adjustable pinhole; D, polepiece of electromagnet; E, magnetizing coil; F, sample; G, x-ray film; H, intensifying screen; I, lead box for absorbing direct beam.

so that only direct radiation from the target should hit the sample. No filter was used to cut out the general radiation.

Superspeed Duplitized x-ray films were used, backed up with a Patterson intensifying screen. In order to absorb the direct x-ray beam passing through the sample, a lead box was provided back of the film and screen, as shown in Fig. 1. The x-ray box and camera were both completely covered with 0.32 cm (1/8″) lead.

The electromagnet used in the first part of the investigation was sufficient to produce from 50 to 75 percent saturation in ingot iron, i. e., field intensities between 25 and 50 gausses. In the second part of the investigation a larger electromagnet was substituted with which complete saturation could be obtained.

4. The Results With Ingot Iron

Two exposures were taken, one using sample A and the other sample C. Preliminary exposures had shown that no trace was obtained on the film with 2 hours exposure, so that 23 hours was used in the above two cases. The patterns obtained were very similar, showing numerous Laue spots due to a few crystals and the general radiation, but in neither case did we find a trace of a circle due to the K_α frequency and randomly oriented crystals. It therefore seemed almost hopeless to expect satisfactory results by this procedure, the obvious reason being the extremely small amount of reflecting material available in the intercrystalline spaces. Another method was therefore sought, and it occurred to the writer that electrolytically deposited iron might serve the purpose.

5. Preparation of Electrolytic Iron Samples

The first procedure tried was that employed by the writer[10] at the University of Illinois and at the Westinghouse Research Laboratory in preparation of electrolytic iron for melting stock. In this method the electrolyte is a ferrous chloride-ferrous ammonium sulphate solution used at room temperature with a current density of 1 amp. per dm.^{2} It yields a very brittle deposit, which is an advantage when it is to be used for melting stock, but in the present case the brittleness was a decided handicap, as it was found impossible to remove the thin deposits without breaking. A method of deposition on zinc followed by removing the zinc from a small portion in the center by electrolysis was only partly successful. The thin film of iron would break on the slightest touch of a camel's hair brush in cleaning away the sludge left after removal of the zinc. However, a few samples were obtained by this method and exposures made, in which the expected circles appeared. Peculiarities in these exposures were traced to imperfections in the iron film, and they were consequently discarded, but they showed that the desired crystal structure could be obtained by electrodeposition and it was only a question of employing a method giving a deposit that would be mechanically strong.

The next method tried was that described by Hughes[11] in which the electrolyte is composed of 600 g. ferrous chloride and 670 g. calcium chloride per liter of water. A current density of 10 amps. per dm.^{2} and a temperature of 100°C were used. For intermittent small scale operation, the $CaCl_2$ was found to be an unnecessary nuisance and was discarded. An excellent deposit was obtained with the ferrous chloride alone. The iron was deposited on zinc and could be peeled off without difficulty, yielding smooth, dense films that could be handled without danger of breaking. Films were prepared ranging in thickness from 0.045 to 0.20 mm. The sizes of the crystals were calculated from the 1/2 width of the x-ray lines[12] giving the dimension of the crystal edge of approximately 135A.

[10] Yensen, Eng. Exp. Sta., Univ. of Ill. Bull.'s No. 72 (1914) and No. 83 (1915).

[11] Hughes, Modern Electroplating, p. 48.

[12] Wyckoff, The Structure of Crystals, 1924, p. 375.

6. Results with Electrolytic Iron Films

A number of samples about 0.1 mm thick were exposed for various lengths of time, 20 to 70 hours, both with and without a magnetic field.

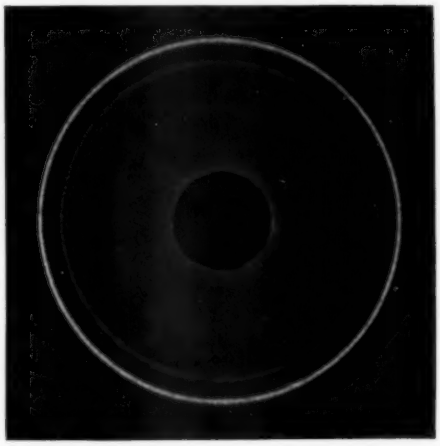

Fig. 2. With zero magnetic field.

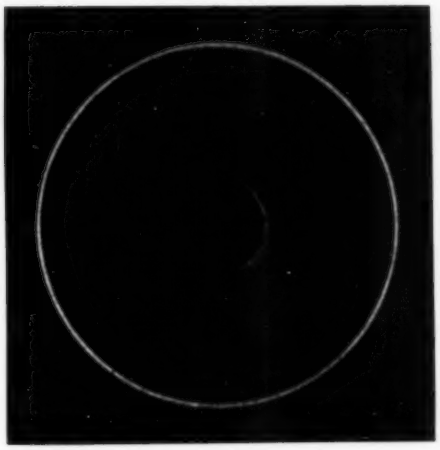

Fig. 3. With field of 50 gausses parallel to diameter 1–2.

X-ray diffraction patterns for electrolytic iron films.

Representative results are shown in Figs. 2 and 3 (Exposures Nos. 13 and 14). Aside from a slight broadening along the vertical axis (traced to the ellipticity of the x-ray beam) occurring both for the magnetized and unmagnetized samples, the circles are uniform, and by direct observation there appears to be no marked difference between the exposures.

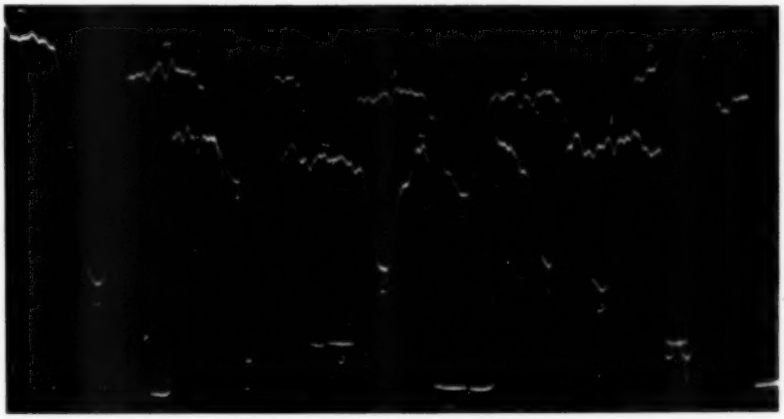

Fig. 4. Photometric analysis of plate shown in Fig. 2.

In order to obtain more reliable data, four exposures were subjected to photometric analysis, using for this purpose the splended microphotometric apparatus of the Mount Wilson Observatory.

The results for Exposures No. 13 and No. 14 are given herewith (Figs. 4 and 5). By this means quantitative data were obtained in regard to relative intensities of lines on any one film.

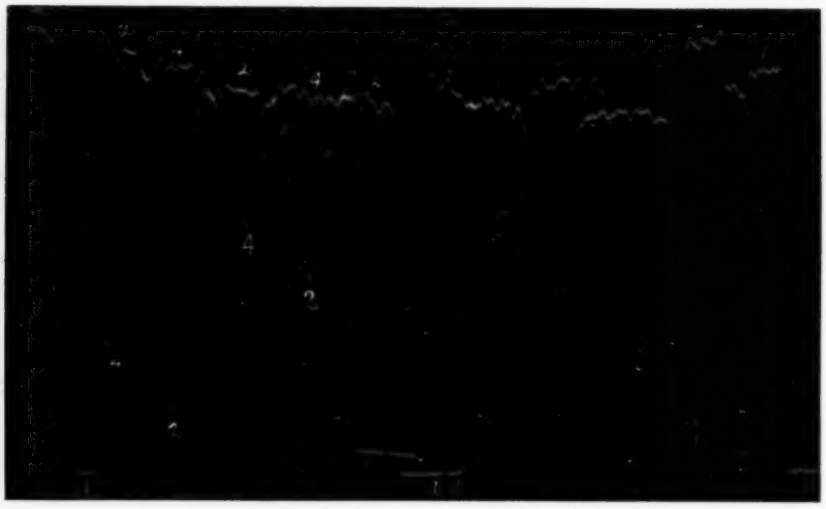

Fig. 5. Photometric analysis of plate shown in Fig. 3.

In the present case the important point was to obtain the ratio, R, of line intensity along the diameter 1–2 parallel to the direction of the magnetic force to that along a diameter perpendicular to it, 3–4, and to compare this ratio for the case of zero force, R_0, with the ratio for the case when the force was applied, R_{mag}.

TABLE I. *Summary of results.* Figures for Nos. 24 and 26 are averages of five values. For these exposures the x-ray box was removed 15 cm from the magnet and the distance between the pinholes was increased by 15 cm. Values for Nos. 13, 14, 20, and 21 were obtained with a ratio of plate travel to film travel = 6.2. For the others the ratio was 2:1.
Diameter 1–2 is parallel to the magnetic force, diameter 3–4 is perpendicular thereto.

Set No.	Exp. No.	Relative Intensity of K_α at 1	2	3	4	1/2 Width (mm) of K_α at 1	2	3	4	Ratio $\frac{1+2}{3+4}$	Mag. Field Intensity gauss	$\frac{R_{mag}}{R_0}$
1	11	42	41	44	45	1.6	1.6	2.0	1.9	0.93	50	0.92
	12	74	63	59	76	1.6	1.7	2.0	2.0	1.01	0	
2	13	50	45	43	48	1.37	1.39	1.93	1.94	1.04	0	1.09
	14	68	71	60	62	1.33	1.33	1.93	1.93	1.13	50	
3	20	45	42	39	40	1.54	1.50	1.99	1.90	1.09	0	1.07
	21	43	44	37	36	1.74	1.78	2.05	1.95	1.17	2600	
4	24	30	26	31	28	1.35	1.37	1.44	1.40	0.95	0	0.92
	26	29	29	35	32	1.36	1.46	1.32	1.40	0.87	2600	
										Mean		1:00 ± .08

The result of the analysis is given in Table I (first 4 rows) the ratio $R_{mag}:R_0$ being 0.92 for Exposures No. 11 and No. 12 and 1.09 for No. 13 and No. 14. On account of the inherent variations in the transparency of the film itself in addition to variations introduced in developing, fixing and rinsing, and also on account of variations due to other causes, like dust particles and possible finger marks, the above ratios may be considered to be as nearly unity as might be expected. A variation of plus or minus 10 percent in microphotometric work is considered reasonable.

The conclusion to be drawn from these results would therefore be that there is no change in orientation of the minute crystals that we are dealing with in these experiments, crystals of the order of 135A, when placed in magnetic fields of moderate strength. But, on account of the possibility, even though remote, that orientation might take place in intense fields, it was decided to repeat the above experiments with a field well above that necessary to produce magnetic saturation in the samples.

7. The Second X-Ray Analyzing Apparatus

Fig. 6 shows the general arrangement of the second apparatus. The same x-ray box was used as in the first set-up, but a powerful electromagnet was employed, capable of producing field intensities above 10,000 gausses

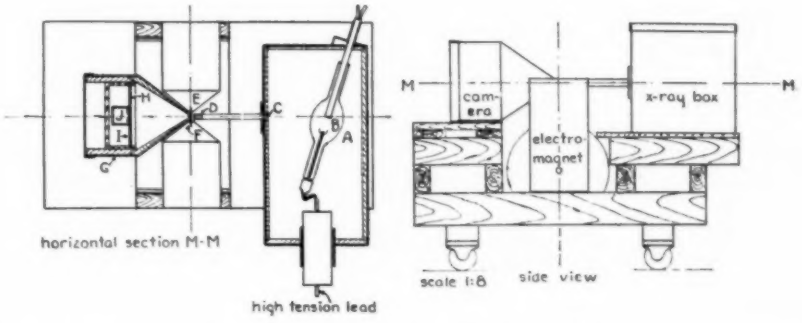

Fig. 6. X-ray analyzing apparatus No. 2. A, x-ray tube; B, molybdenum target; C, fixed pinhole; D, adjustable pinhole; E, electromagnet polepieces; F, sample; G, camera; H, photographic film; I, intensifying screen; J, lead box for absorbing direct beam.

between the pole pieces. It was not pushed beyond 2600 gausses, however, in the present experiment, as iron becomes saturated when placed in a field with an intensity of 1000 gausses. A conically shaped camera was constructed in order that the film might be placed as closely as possible to the sample, the distance being approximately 15.6 cm.

8. Results Obtained with Saturation Fields

Fig. 7 (Exposure No 20, zero magnetic field) and Fig. 8 (Exposure No. 21, field intensity of 2600 gausses) were obtained with sample No. 33_2, (0.045 mm thick), and these show uniform circles. The films were photometered with the result given in Table I, 5th and 6th row. The ratio R_{mag} to

R_0 in this case is 1.07, showing that there is no preferred orientation of the crystals even with a field intensity of 2600 gausses. On the other hand, a comparison between Figs. 7 and 8 in regard to width of lines reveals a broadening of the lines along the horizontal diameter in Fig. 8 (field on), amounting to about 15 percent. It was shown by direct experiment that this broad-

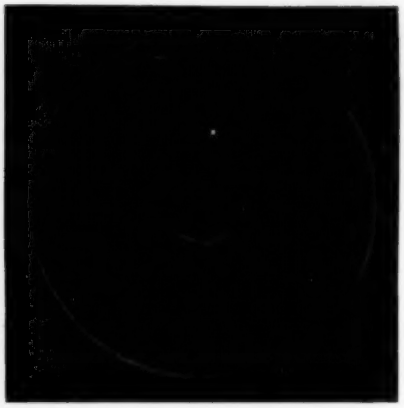

Fig. 7. With zero magnetic field.

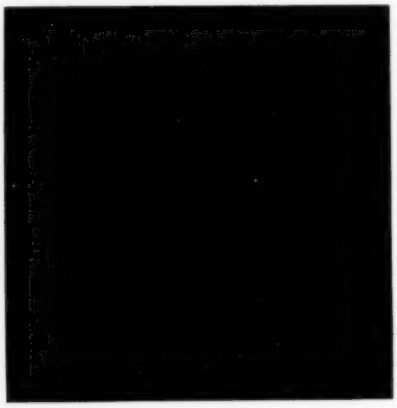

Fig. 8. With field of 2600 gausses parallel to diameter 1–2.

X-ray diffraction patterns for electrolytic iron films.

ening was due to the deflecting effect of the stray magnetic field from the large magnet on the cathode electron stream, and has no connection with the crystal structure of the sample.

9. Eliminating the Effect of the Stray Field on the X-ray Beam

It seemed, however, desirable to obtain a positive proof that the magnetic field produces no change whatever in the crystal structure, and for this purpose it was obviously necessary to eliminate the stray magnetic field in the x-ray tube. An attempt to accomplish this by surrounding and lining the x-ray box with ingot iron sheet made the conditon worse, as the sheets were too thin to produce effective shielding. A solid iron box would undoubtedly have been the ideal solution, but in lieu of this the x-ray box was moved 15 cm away from the magnet and the distance between the pinholes increased by this same amount. By this means the effect of the magnetic field was practically eliminated. An obvious disadvantage of the arrangement was that much longer exposures were needed both because of the smaller effective aperture and of the greater distance from the x-ray tube to the sample. The next two exposures, No. 24 (zero field) and No. 26 (with field) were therefore run for 48 hours, and even with this long exposure the circles were rather weak. In analyzing these films with the microphotometer five adjacent points along each diameter were therefore used and the results averaged. These averages are given in Table I, in the last two rows. While there is not

perfect agreement in the 1/2 width even in this case, it is very much better than in the previous case, the change in width now being +1, +6, −9 and 0 percent respectively. The ratio for this case is $R_{mag}/R_0 = 0.92$, when using the relative intensities of the lines only. Again, in this case this result may be regarded as unity.

It is interesting to note that if the four sets of results are averaged a value is obtained that by fortunate coincidence is $R_{mag}/R_0 = 1.00$, but the variation is ± 0.08, so that the result must be written in the form $(R_{mag}/R_{av.}) = 1.00 \pm 0\ 08$.

If, instead of using the relative intensities only, the areas under the photometric curves are used, or, as a close approximation, the products of the maximum relative intensities and the 1/2 width, the results of Table II are obtained. Sets Nos. 1 and 2 give approximately the same result as in

TABLE II. *Summary of results.* The data from Table I is used to calculate the relative integrated intensity (relative intensity × 1/2 width).

Set No.	Exp. No.	Rel. Int. × 1/2 Width at 1	2	3	4	1+2 / 3+4	Field Intensity Gausses	R_{mag}/R_0
1	11	68	65.5	89	85	0.77	50	0.92
	12	119	107	118	152	0.835	0	
2	13	69	62	84	94	0.735	0	1.08
	14	90	94	116	120	0.780	50	
3	20	69	63	78.5	77	0.85	0	1.22
	21	75.0	78.5	76	71.2	1.04	2600	
4	24	40.4	36.3	46	39.2	0.91	0	1.00
	26	39.3	42.8	45.7	44.7	0.91	2600	

Mean of all four sets: 1.05
Exclusive of the Erratic Set No. 3: 0.994 ± 0.08

Table I, but Set No. 3 is very erratic on account of the abnormal width of the lines, as described above, giving a ratio $R_{mag}/R_0 = 1.22$, while Set No. 4 gives a ratio 1.00. If Set No. 3 is excluded, the mean of the three other sets is $R_{mag}/R_0 = 0.994 \pm 0.08$, or practically the same as in Table I. From these results it therefore seems reasonable to draw the conclusion that there is no orientation of the crystalline aggregates in iron when the sample is subjected to a magnetic force even sufficient to produce magnetic saturation.

This work was done at California Institute of Technology while on leave of absence (1925–27), and the writer wishes to express his thanks to Dr. R. A. Millikan for placing the facilities of the Norman Bridge Laboratory at his disposal. The writer also wishes to express his appreciation to Dr. S. J. Barnett, Dr. R. G. Dickinson, Dr. J. W. DuMond, Dr. W. V. Houston, Dr. L. Thomassen and Dr. F. Zwicky for help with apparatus, suggestions or discussion of results.

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TIME-LAG IN MAGNETIZATION

By Richard M. Bozorth

Abstract

An investigation has been made of the time-lag in magnetization in a permalloy wire to determine whether lag can be satisfactorily accounted for as due to eddy-currents alone or whether permalloy shows a marked magnetic viscosity such as has been observed by Ewing in iron wires. *Eddy-current lag* has been calculated approximately in a manner which takes into account the changing slope of the magnetization curve. A comparison of the calculated and observed magnetization-*vs*-time curves indicates that the effect is well accounted for as eddy-current lag alone. The eddy-current lag has also been calculated for an iron ring, for which the time-lag has been reported recently in a number of papers by Lapp. The time-lag which he observed is satisfactorily accounted for as eddy-current lag instead of as magnetic viscosity as he had supposed.

1. Introduction

WHEN a magnetic force is applied to a ferromagnetic body an appreciable time is required for the magnetization to reach its final state. One contributing cause for this time-lag in magnetization is, of course, the opposing magnetic force produced by eddy-currents within the body. Time-lag has been observed, however, which cannot well be accounted for as due to eddy-currents. For example, the measurements made by Ewing[1] with an iron cylinder 4 mm in diameter show that the magnetization changes appreciably even after the applied magnetic force has been constant for over ten minutes, as shown in Fig. 1. Now Wwedensky[2] has calculated the time rate of change of magnetization delayed by eddy-currents, for the case in which dB/dH, the rate of change of magnetic induction with magnetic force, is constant, and his results indicate that to explain Ewing's results as eddy-current lag we must assume for his sample a value of dB/dH of over 10^7, whereas at the steepest part of the *B-vs.-H* curve for iron a reasonable value for dB/dH is 25,000. This phenomenon, the nature of which is still obscure, is best called "magnetic viscosity," after Ewing.

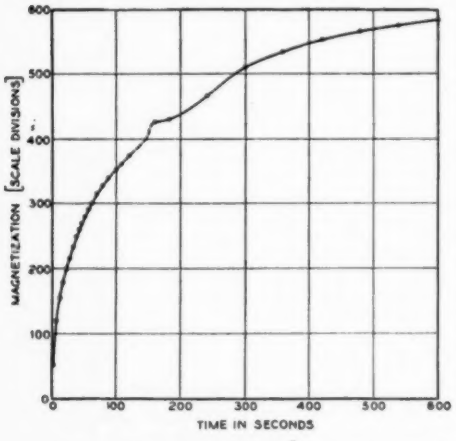

Fig. 1. Magnetic viscosity observed by Ewing, not explicable as due to eddy-currents. When this experiment had been under way for 150 seconds the laboratory door slammed, producing temporarily a rapid increase of magnetization as shown by the hump on the curve.

[1] J. A. Ewing, Proc. Roy. Soc. **A46,** 269–286 (1889).
[2] B. Wwedensky, Ann. d. Physik [4] **64,** 609–620 (1921).

Many experimenters have observed and described magnetic lag.[3] In some cases it seems evident that the lag is due to eddy-currents, and Smith[4] and Wwedensky[5] have interpreted their own results in this way. To determine whether certain strikingly large time-lags, which have been observed in these laboratories in measuring permalloy wires, could all be accounted for as due to eddy-currents or whether some of the effects must be ascribed to magnetic viscosity, the writer undertook the experiments described in Section 3 below. Having found that eddy-currents suffice to explain the lag observed in permalloy, the writer was then led to question the conclusions of Lapp,[6] who has recently made extensive measurements of magnetic lag in iron rings, and who regards the phenomenon which he has studied as magnetic viscosity and not as eddy-current lag. It is shown in Section 4 below that his measurements can be satisfactorily explained as due to eddy-currents alone.

2. Calculation of Eddy-Current Lag

When the relation between magnetic induction, B, and magnetic force, H, is linear, the change in B produced by a rapid change in H at the time $t=0$ can be calculated as a function of time for a cylindrical sample by taking into account the magnetic fields due to the eddy-currents produced by the changing induction. According to an approximate calculation by Rayleigh,[7] letting b represent the fraction of the total change in B which occurs after the time t,

$$\ln b = -\frac{1.44t}{\pi r^2 \sigma dB/dH},$$

where r is the radius of the cylinder and σ is the electrical conductivity in absolute electromagnetic units. More recently Wwedensky[2] has calculated exactly the relation between b and t when dB/dH is constant and has expressed his results in the form of a table. Rayleigh's relation agrees closely with Wwendesky's table for values of b between 0 and 0.9, and approximately for values of b between 0.9 and 1.0.

If dB/dH changes during the change in induction, no accurate method is available for calculating the time lag. A rough estimation of the magnitude of the effect can be made, however, by assuming that Rayleigh's equation holds for each element of the B-*vs.*-H curve, that is,

$$d \ln b = -\frac{1.44dt}{\pi r^2 \sigma f(B)},$$

[3] An extensive bibliography is given by C. Lapp, Ann. de physique [10] **8,** 278–395 (1927). An important addition to this list is H. Tobusch, Ann. d. Physik [4] **26,** 439–482 (1908).

[4] A. W. Smith, Phys. Rev. [2] **9,** 419–424 (1917).

[5] B. Wwedensky, Ann. d. Physik [4] **66,** 110–129 (1921).

[6] C. Lapp, Jour. phys. rad. [6] **4,** 349–369 (1923); **4,** 169S (1923); **6,** 166–176 (1925); **7,** 230–239 (1926); **8,** 29S–30S (1927); Rev. gen. elec. **15,** 88 (1924); Ann. de physique [10] **8,** 278–395 (1927); Rev. de met. **24,** 496–508 (1927); Rev. scient. **65,** 631 (1927).

[7] Lord Rayleigh, Rep. Brit. Assn. **52,** 446–447 (1882).

where $f(B)$ gives the value of dB/dH for each value of B (or b), and is determined from the B-*vs.*-H curve. The time, t, for any value of b, is then given by the expression

$$t = 2.2\sigma r^2 \int_b^1 \frac{dB}{dH}\frac{db}{b},$$

in which the integration is performed graphically. This expression is based on the assumption that the flux is uniform over the cross-section of the wire. The effect of the non-uniformity of distribution, which really exists, can be predicted qualitatively, and will be discussed in the next sections where experimental and calculated values of t are compared.

3. Measurements on a Permalloy Wire

The sample of permalloy with which time measurements were made contained by analysis 78.1 percent Ni and 21.3 percent Fe, and a little Mn. The diameter of the sample was 0.102 cm and its length 67 cm. It was enclosed in a permalloy yoke[8] and the magnetic measurements were made by the ballistic method using a galvanometer with a half-period of seven seconds.

For measuring the residual change in induction, bB, a change in magnetic force was produced in the magnetizing coil surrounding the sample, and a measured time, t, afterwards the search coil was connected to the galvanometer. These magnetizing and galvanometer connections were each made by relays which were operated by two metal brush contacts on a rapidly rotating shaft having alternate conducting and insulating segments. Other relays prevented the operation of the relay controlling the galvanometer circuit until the relay controlling the magnetizing circuit had already closed, and still others held these relays closed once they had been tripped. The relays were put into operation by closing a switch connecting them to a battery, and after the galvanometer deflection was observed they were all released by raising this switch.

The time which elapsed between the closing of the two circuits was calculated from the rate of rotation of the shaft, which was measured by a tachometer and read directly on a voltmeter in revolutions per second. One of the brushes making contact with this shaft could be moved around the shaft with respect to the other. The zero position of this brush—that is, its position when the magnetizing and the galvanometer circuits closed simultaneously ($t=0$, $b=1$) —was carefully checked in a separate circuit in which a slight departure from the zero position caused a deflection of a galvanometer, and correct adjustment caused none. Special care was necessary in insulating the contacts in the relay controlling the galvanometer circuit.

[8] O. E. Buckley and L. W. McKeehan, Phys. Rev. [2] **26,** 269 (1925). This yoke should have little or no effect on the decay of eddy-currents in the sample, for the magnetic flux which passes through it is divided among 10 cylindrical rods. In each of these rods r^2B, which determines the strength of the eddy-currents, is one-tenth of what it is in the sample itself, so that the currents in the yoke should die out much faster than in the sample. No direct experimental test of this point was made.

The time necessary for the magnetic force to attain a constant value was computed from the known resistance and inductance of the circuit to be negligibly small; less than 5 percent of the total change in magnetic force occurred after 10^{-4} sec.

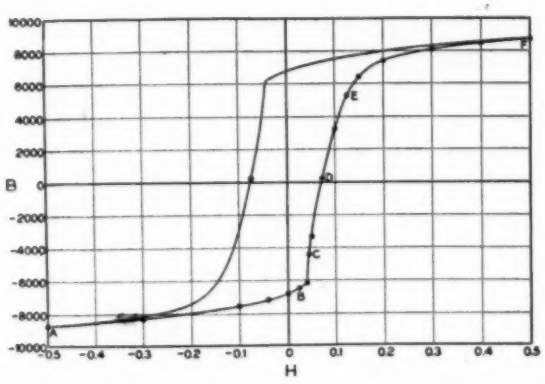

Fig. 2. Hysteresis loop for permalloy containing 78 percent nickel.

The hysteresis loop for a maximum magnetic force of 0.5 gauss is shown in Fig. 2. All lag measurements were made with the magnetic forces chang-

TABLE I. *After the magnetic field has been constant for t seconds, the magnetic induction changes by the fraction b of the total change in induction from A to E in Fig. 2.*

t	*b*	*t*	*b*	*t*	*b*
0.000	1.000	0.020	0.609	0.15	0.0726
.001	.920	.030	.502	.20	.0263
.002	.872	.050	.372	.25	.0090
.005	.808	.075	.262	.30	.0044
.010	.740	.100	.194	.40	.0028

ing from -0.5 gauss to various positive values marked on the hysteresis loop with letters. Table I shows the results obtained when the final value

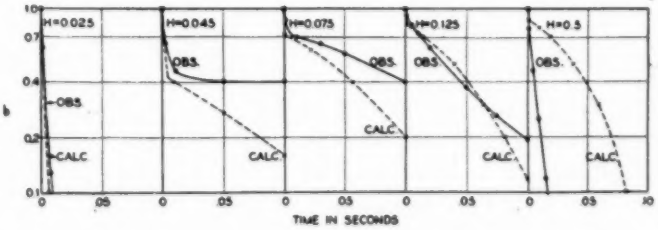

Fig. 3. Time lag in magnetization in a permalloy wire 1 mm in diameter, containing 78 percent nickel. The letter *b* represents the fraction of the total change in flux which takes place after a certain measured time.

of the magnetic force was $+0.125$ gauss. The log *b-vs.-t* curves are shown as solid lines in Fig. 3 for various changes in B, and the dashed lines are the corresponding curves calculated as described in Sec. 2 above.

Comparing the calculated and observed curves, it will be noticed that when the magnetic state changes from that represented by the point A to that represented by the point B ($H=0.025$) the induction changes through various values for which dB/dH continually increases. Although in calculating the time lags it is assumed that the whole cross-section of the sample is in the same magnetic state, in reality the outside approaches its final state more quickly than the inside and so dB/dH is greater in the outer layers than is implicitly assumed in the calculation. For a given value of b, then, the measured times will be greater than those calculated. When the opposite situation occurs, and the magnetic state of the sample changes from A to F ($H=0.5$) so that during most of the time dB/dH decreases as the induction changes, the calculated times will be too large. For changes such as A to E ($H=0.125$) the calculated times may be expected, because of the simplifying assumption of uniform flux distribution, to be sometimes too small and sometimes too large. All these expected differences are found between the calculated and experimental curves shown in Fig. 3. It is difficult at first to see how the slope of the flat portion of the second observed curve in the figure can be so different from that of the calculated curve. It seems probable that the large values of dB/dH determined from the hysteresis loop near the point C are in error, and that their true values are even greater. This discrepancy may be due to several causes besides the obvious error in determining a slope so large. For example, if the coercive forces for different parts of the wire are but slightly different, the superpositon of their B-*vs.*-H curves shows that the measured value of dB/dH may be too small by a large factor if dB/dH is already large. Another contributing factor may be the discontinuities in magnetization which as Barkhausen[9] has shown, occur in that part of the magnetic cycle for which dB/dH is large.

4. Measurements by Lapp on Iron Rings

Recently Lapp[6] has measured time-lag in rings of pure iron. The cross-sections of these rings were rectangular and varied in area between 0.1 and 1.0 cm^2 in the various samples used. Although Lapp states that induced currents are negligible[10] when the cross-sectional area is 1 cm,^{2} nevertheless the calculations described below indicate very definitely that his measurement of change of induction with time, and also of the effects of cross-sectional area and shape and of temperature on the induction-*vs.*-time curves, are satisfactorily explained as due to eddy-currents.

Variation of induction with time. Fig. 4 shows the hysteresis loop plotted from Lapp's tabulated data for a ring having a cross-section of about 2.0×0.4 cm,^{2} and Fig. 5 his observed values of log b and t (solid lines) and my values (dashed lines) calculated as described in Section 2. The differences between the calculated and observed curves are of the same nature as those discussed above in connection with the measurements on the permalloy

[9] H. Barkhausen, Phys. Zeits. **20**, 401–403 (1919).
[10] C. Lapp, Ann. de physique [10] **8**, 280 (1927).

wire, and seem to be caused by the simplifying assumption made in the calculation. It is at once obvious from the form of both the observed and

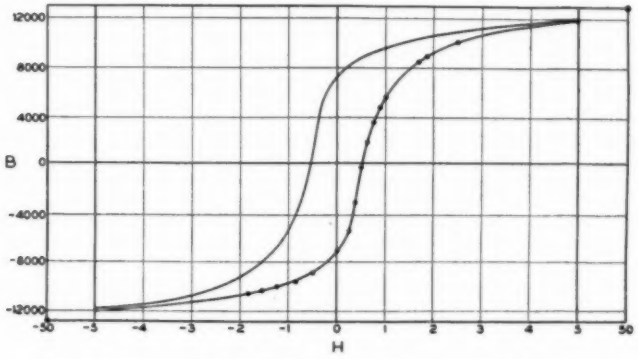

Fig. 4. Hysteresis loop for pure iron according to Lapp.

calculated curves, why it is that when Lapp extrapolated his curves to $t=0$ he found a value of b less than unity; for the smallest time which Lapp

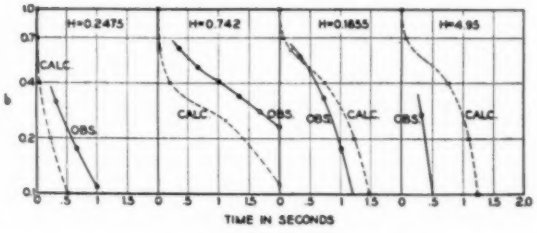

Fig. 5. Time lag in magnetization in a ring of pure iron having a cross-sectional area of 0.82 cm², as measured by Lapp (solid lines) and as calculated by the writer (dashed lines).

measured was 1/3 second, and the calculated curves show that for smaller values of t the curves bend upward ending at the point $t=0$, $b=1$.

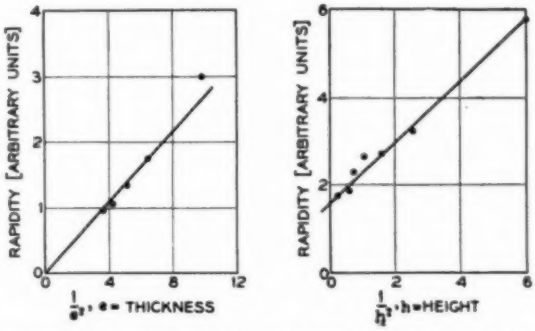

Fig. 6. Variation of rapidity with the thickness and height of the ring sample, according to measurements made and plotted by Lapp.

Effect of cross-sectional area and shape. Lapp's measurements show the effect of the area and shape of the sample on the "rapidity," β, which may

be defined in accordance with Lapp's equation as the slope of the ln*b*-*vs*.-*t* curve. Fig. 6 shows Lapp's curves of rapidity-*vs*.-thickness, *e*, and rapidity-*vs*.-height, *h*, indicating that the rapidity varies inversely as the squares of the thickness and of the height. Taking account of the rectangular cross-section of the sample, analysis shows[11] that $1/r^2$ in the equation for circular cross-sections may be replaced by $(h^2+e^2)/h^2e^2$. This factor, it will be noted reduces to $1/e^2$ for thin sheets ($h>>e$). Now assuming the lag to be caused by eddy-currents, the rapidity can be calculated as a function of thickness and height and compared with Lapp's experimental data. Fig. 7 shows the

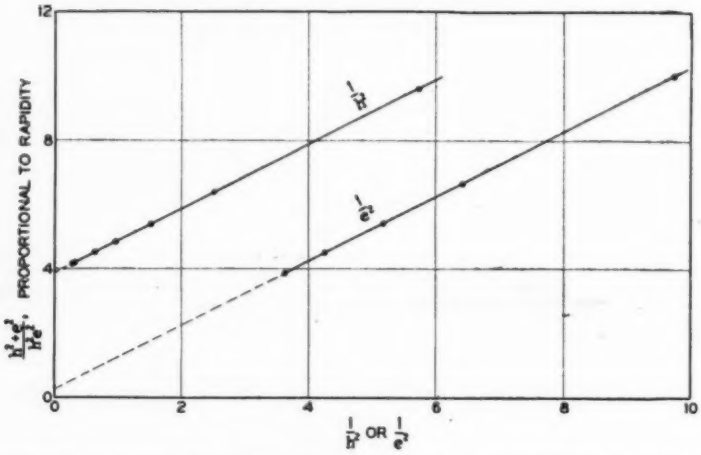

Fig. 7. Calculated variation of rapidity with thickness, *e*, and height, *h*, of a ring sample. Compare the straightness of these lines with that of the experimental lines of Fig. 5.

result of such a calculation using the values of *e* and *h* for Lapp's cores, and comparison with Fig. 6 shows that the relations between cross-sectional dimensions and rapidity which he observed are those to be expected from my analysis.

Inspection of the factor $(h^2+e^2)/h^2e^2$ indicates that for similar cross-sections (h/e=constant), the rapidity varies inversely as the area of the cross-section. On the other hand, if h/e is large and h is kept constant while e is varied the rapidity varies with the square of the area of cross-section as Lapp has stated. It is clear that no general statement can be made regarding the dependence of the rapidity upon the area of cross-section.

Effect of temperature. The dependence of rapidity upon absolute temperature observed by Lapp ($\beta \propto T^2$) can also be explained if the resistivity, $1/\sigma$, which we have seen is proportional to β, is nearly enough proportional to T^2. To show how nearly the relation $1/\sigma \propto T^2$ is satisfied experimentally, the data[12] for pure iron are plotted in Fig. 8 and a straight line drawn for which this relation is exactly satisfied.

[11] Assuming that the current paths are rectangular, Dr. J. J. Gilbert of these laboratories has derived this factor depending upon the dimensions of the cross-section.

[12] J. Dewar and J. A. Fleming, Phil. Mag. [5] **36**, 271 (1893); L. Holborn, Ann. d. Physik [4] **59**, 145–169 (1919); W. Meissner, Zeits. f. Physik **38**, 647–658 (1926).

It appears probable that Lapp's observations on the effects of aging and annealing of iron, and his experiments on cobalt and nickel, can also be explained as due to eddy-currents, the different behavior with various treatments and materials being attributed to the different character of their *B-vs.-H* curves, and perhaps to the magnetic non-homogeneities produced by heat treatments such as quenching.

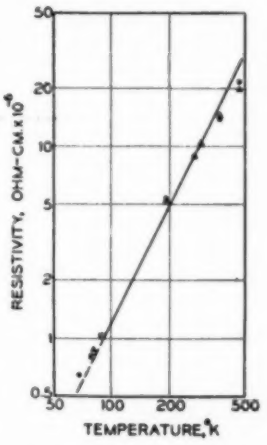

Fig. 8. Resistivity of iron at various absolute temperatures. The data are those of Dewar and Fleming (circles), Holborn (triangles), and Meissner (squares). For the straight line the resistivity is exactly proportional to the square of the absolute temperature, the relation necessary to explain the variation of rapidity with temperature observed by Lapp.

5. Magnetic Viscosity

The nature of the phenomenon of magnetic viscosity, exemplified by the experiments of Ewing, still remains obscure. It is barely possible that slight statistical fluctuations in the supposedly steady current from the battery, or in a superposed magnetic field, could account for these observations. Another possibility is that the sample is continually subjected to slight vibrations which, as Ewings's data show, would produce a change in induction in the right direction.

To test this latter point, to find the course of the induction vs. time curve when the sample was continually vibrated, a 4 cm length of 0.5 mm soft iron wire was placed in a magnetometer[13] and an ordinary electric buzzer attached rigidly to the framework on which the magnetometer was mounted. The field was changed rapidly, with the buzzer not operating, to a new value such that dB/dH was constant over a considerable region; then the buzzer was operated for various lengths of time and the corresponding deflections of the magnetometer noted. The results are shown in Fig. 9, curve *A*, where the logarithms of the deflections (1 unit corresponds to 0.01 gauss) are plotted against the logarithms of the time. The fact that the curve is a straight line over a large part of its course shows that the nature of the phenomenon is entirely different from that of eddy-current lag,[14] and suggests that it is very similar to the effect observed by Ewing, which is replotted in Fig. 9, curve *B*, for comparison.

It is very doubtful, however, whether the lag observed by Ewing could have been due to external mechanical shock, because the shock necessary to reproduce approximately Ewing's magetization vs. time curve is so large that it could not well have escaped his notice. The most reasonable supposition, therefore, is that the phenomenon that Ewing observed should be properly termed magnetic viscosity, and the suggestion is made that it is

[13] R. M. Bozorth, J.O.S.A. & R.S.I. **10**, 591–598 (1925).

[14] Assuming any reasonable value for the final induction, the log *b-vs.-t* curve departs widely from a straight line.

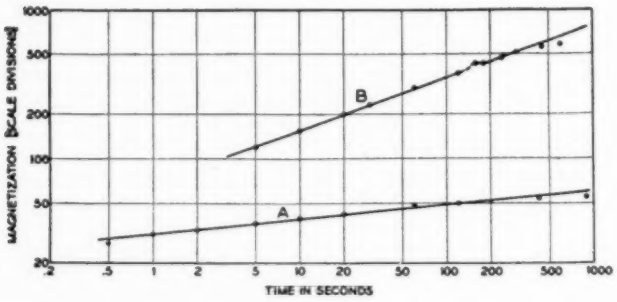

Fig. 9. Curve *A* shows the effect of continuous mechanical vibration on magnetization as a function of time. In curve *B* Ewing's data of Fig. 1 are replotted to show that in this case, as well as when the sample is vibrated, the magnetization vs. time curve is a straight line when plotted with double logarithmic scales.

caused by the disturbances of unstable configurations of molecular magnets by thermal vibrations, in much the same way that such configurations are disturbed by mechanical vibrations produced from the outside.

BELL TELEPHONE LABORATORIES, INCORPORATED,
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THE DIAMAGNETIC LAYER OF THE EARTH'S ATMOSPHERE AND ITS RELATION TO THE DIURNAL VARIATION OF TERRESTRIAL MAGNETISM*

By Ross Gunn

Abstract

Anisotropic conductivity of upper atmosphere due to presence of earth's magnetic field.—An investigation of the motion of ions and electrons in the region of long free paths shows that the electrical conductivity in the direction of the earth's magnetic field is that predicted by simple theory. The conductivity in a direction at right angles to the magnetic field and in the direction of the applied electric field is zero while the pseudo conductivity at right angles to both is finite and the mechanism such that ions of both kinds are swept in the same direction. As a consequence of this situation it appears that large circulating currents in the upper atmosphere of the type assumed in present theories of the diurnal terrestrial magnetic variations are hardly possible.

Theory of the diurnal magnetic variation based on diamagnetic effect of ions in upper atmosphere.—A theory of the diurnal magnetic variation is worked out which explains quantitatively the major phenomena in terms of the diamagnetic effect produced by ions spiralling about the earth's magnetic field. The diamagnetic intensity of magnetization of the upper atmosphere in the region of long free paths is found to depend upon the total number of ions of all kinds per cubic centimeter; their mean kinetic energy and the impressed magnetic field. The maximum calculated diurnal magnetic variation as a function of latitude was found to agree in form with observation. The average maximum number of ions of all kinds per cm^3 in the upper atmosphere was then computed from observed magnetic data and found to be approximately 5×10^{10}, a number not inconsistent with the ionic density inferred from data derived from radio phenomena.

IT HAS been long recognized that the solar and lunar components of the diurnal magnetic variation of the earth are intimately related with the radiant energy of the sun. The maximum magnetic effects usually occur near mid-day local time and are more pronounced during the summer months. Radio and other data have led to the assumption of a highly ionized conducting layer at some distance above the earth's surface which, it has been assumed, is due to ionization by the ultra-violet light of the sun, high speed corpuscles, etc.

A theory of the diurnal magnetic variation of the earth's field originally proposed by Balfour Stewart and examined in great detail by Schuster[1] and Chapman[2,3] depends on the circulation of electric currents in a non-uniform conducting layer situated somewhere in the upper atmosphere. The electric currents are assumed to be due to electromotive forces induced in the con-

* Released for publication by Navy Department.

[1] Schuster, Phil. Trans. Roy. Soc. **A208,** 163 (1908).

[2] Chapman, The Solar and Lunar Diurnal Variation of Terrestrial Magnetism, Phil. Trans. Royal Soc. **A218,** 1 (1919).

[3] Chapman, Ionization in the upper atmosphere, Roy. Meterol. Soc. **52,** 225 (1926).

ducting layer by the action of tidal and thermo-tidal motions of the atmosphere. Chapman[3] has made a calculation of the conductivity necessary to account for the observed effect assuming that the current flows in the direction of the induced electric field. This view is undoubtedly correct at low altitudes where the free path of the ion is short but is open to serious objection in regions where the free path is long. Radio data seem to indicate that the ion and electron banks are located in the region of long free paths. Moreover, Hulburt's[4] calculations on the upper atmosphere show that the number of electrons or ions available in the region of short free paths is entirely inadequate to explain the currents necessary to account for the observed magnetic variations.

A critical examination of the properties of the upper ionized or Kennelly-Heaviside layer shows that it differs from a simple conducting layer in two very important respects. First, the electrical conductivity is anisotropic. Second, the layer is strongly diamagnetic. The presence of these two effects modifies profoundly present theories of the diurnal magnetic variations of the earth's field.

A consideration of the conditions existing in the upper atmosphere shows that on a winter day at altitudes as low as 140 km any electron in thermal equilibrium with the layer will spiral around the earth's magnetic field some 3000 times before colliding with a molecule while even the heaviest ion will make two revolutions before colliding. The direction of rotation of the ions or electrons is always such as to reduce the impressed field, irrespective of the sign of the charge on the ion. If there are a great number of these ions their demagnetizing effect may be considerable.

In the presence of an electric field at right angles to the magnetic field there is superimposed on this spiral motion a quasi-periodic motion by which the ion advances along a path at right angles to both the electric and magnetic fields but has no net motion in the direction of the electric field.

The conductivity of the ionized layer may be computed by considering the equations of motion of an ion under the influence of an electric and a magnetic field. In a system of rectangular coordinates let the direction of the magnetic field H be along the Z axis and let an electric field be impressed in such a manner that it has components E_x, 0, E_z, then if m is the mass of the ion, e its charge, the equations of motion are:

$$md^2x/dt^2 = E_x e - He\,dy/dt \tag{1}$$

$$md^2y/dt^2 = He\,dx/dt \tag{2}$$

$$md^2z/dt^2 = E_z e \tag{3}$$

The velocities of the ion are then determined by assuming the initial velocity components in the x, y and z directions to be U_0, V_0 and W_0, respectively. The velocity components of the ions on integration are as follows:

$$V_z = (E_z e/m)t + W_0 \tag{4}$$

$$V_y = E_z/H - U_0 \sin \omega t + V_0 \cos \omega t - (E_z/H) \cos \omega t. \tag{5}$$

$$V_x = U_0 \cos \omega t + V_0 \sin \omega t + (E_z/H) \sin \omega t \tag{6}$$

[4] E. O. Hulburt, Phys. Rev. **31**, 1018 (1928).

where

$$\omega = -eH/m \tag{7}$$

For infinitely long free paths the average velocities become:

$$\overline{V}_x = \infty \; ; \; \overline{V}_y = E_x/H \; ; \; \overline{V}_z = 0 \tag{8}$$

Thus remembering that the conductivity on the simplest basis is given by:

$$\sigma = Ne\overline{V}/E \tag{9}$$

where N is the number of ions, e their charge, $\overline{V}$ their average migration velocity and E the impressed electric field. The expressions for the conductivity become approximately the following, remembering that the free path is not strictly infinite:

$$\sigma_x \doteq Ne\lambda/2mu \; ; \; \sigma_y \doteq Ne/H \; ; \; \sigma_z \doteq 0 \tag{10}$$

A restricted definition of σ_y must be made since it is the conductivity in a direction at right angles to the impressed electric field.

The most important consequence of the above considerations is that the conductivity in the direction of the impressed electric field which itself is perpendicular to the magnetic field, approaches zero. Thus, large circulating currents of the type originally suggested by Stewart seem to be very improbable except perhaps in regions of short free path where the ionic densities are small. Preliminary examination seems to indicate that such an anisotropic conductivity may assist in explaining the diurnal variation of the earth's electric field.

The spiralling of the electrons and ions about the earth's magnetic field due to their thermal agitation or mass motion of the associated neutral molecules offers an explanation of the diurnal magnetic variations which appears to fit the observed facts very well.

It will be assumed in this paper that the regions in the upper atmosphere are highly ionized by ultra-violet light or by some other agent. In particular, we shall confine our attention to those ionized regions where the free path of the ion is greater than the diameter of the circle described by the ion moving freely in the earth's magnetic field. We shall assume this layer to be ionized but nearly neutral and shall investigate the field produced on the surface of the earth by the presence of such ions which are maintained in motion by thermal agitation or by momentum communicated to them by mass motion of the associated neutral molecules. To explain certain minor phenomena we shall assume the presence of certain small radial electric fields which may be modified directly or indirectly by some outside influence, presumably by corpuscles shot off from the sun.

Schroedinger[5] has examined the theory of diamagnetism due to free electrons in metals which tend to spiral around the impressed magnetic

[5] Schroedinger, Wien Ber. **66**, 1305 (1912). Also Bulletin No. 18 of National Research Council.

field, and it can be readily shown that his result for long free paths agrees (after considerable reduction) with the simple derivation below except for a numerical factor due to the different method of averaging. Bohr (thesis) and Van Leeuwen[6] have examined Schroedinger's work and concluded that if reflections of the electrons at the boundary of the metal were taken into account then the net diamagnetic effect outside the conductor would be zero. These objections do not hold at the boundary of the diamagnetic region situated at high altitudes, since the free paths are very long and the transition layer is thousands of times deeper than the circular path described by even the heaviest ion. A calculation of this diamagnetic effect due to ions having a long free path may be made as follows: The magnetic moment M due to one ion describing a circular orbit of area S in time τ is:

$$M = eS/\tau \tag{11}$$

where e is in e.m.u. Moreover, since the centrifugal force and the magnetic force on the ion are equal we may write:

$$mV^2/r = HeV \tag{12}$$

where m is the mass of the ion, V is the component of velocity perpendicular to the magnetic field, e its charge, H the impressed magnetic field and r the radius of the circular path. Solving

$$r = mV/He.$$

Now

$$S/\tau = rV/2 = mV^2/2He \tag{14}$$

So

$$M = mV^2/2H \tag{15}$$

Now, if there are N ions per cm^3, then the intensity of magnetization becomes:

$$I = -NmV^2H_1/2H \tag{16}$$

where H_1 is the unit vector in the direction of the impressed vector field. If one temporarily discards the possibility of mass motion of the neutral molecules associated with the ion bank, and takes the absolute temperature of the bank to be T, then the above relation may be transformed to $I = -(2N\epsilon T/3H)H_1$, where ϵ is the constant of molecular energy. It follows from this expression for I that the diamagnetic effect in the upper layers will vary greatly from midnight to noon local time, since the number of ions per cm^3 will increase greatly under the influence of the ultra-violet light of the sun. Moreover, the longer radiations will raise the absolute temperature of the region by a factor of nearly two. Thus, for a given value of H the intensity of magnetization of the diamagnetic layer will increase greatly in the daytime.

The cause of the solar component of the magnetic variation may then be attributed to a diamagnetic layer or cap covering the terrestrial hemisphere

[6] Van Leeuwen, Jour. d. Physique **2**, 361–377 (1921).

that faces the sun. The earth in its rotation brings given points on its surface successively under the influence of this diamagnetic cap, and then well away from it. The maximum effect of the diamagnetic cap would be expected to be at the point on the earth's surface which is nearly immediately under the region of maximum diamagnetic intensity. Experiment seems to indicate that this maximum intensity is overhead about two hours before noon local time.

In order to make a rough quantitative study of the effect we shall simplify the computation by assuming that the diamagnetic layer is a shell or cap located between 150 and 180 km above the earth's surface; that the magnetic poles coincide with the geographic poles; that the magnetic field is such as would be produced by a small magnet placed at the center of the earth and producing the observed field at the equator and assuming further that the temperature is uniformly 300°K and the layer is 30 km thick. Under these conditions, which will not greatly modify the general result, the field variation at the equator at noon during equinox may be computed in terms of the total number of ions of all kinds per cc. It is reasonable to assume that the number of ions per cc is proportional to the intensity of the incident sunlight or

$$N = N_0 \cos \phi + \delta \tag{17}$$

where N_0 is the number of ions per cc at the equator at noon, ϕ is the angular latitude and δ is the average number of residual ions left during periods of darkness. We are interested here only in the variation of the field so this term will be neglected. The intensity of the field has been taken as that due to a small magnet placed at the center of the earth, therefore the magnetic field H at any latitude may be represented by:

$$H = H_0(1+3 \sin^2 \phi)^{1/2} \tag{18}$$

where H_0 is the magnetic field at the equator. Thus, an approximate expression for the intensity of magnetization at noon during equinox for any latitude is determined.

$$I_\phi = -\frac{2N_0 \epsilon T \cos \phi \, H_1}{3H_0(1+3 \sin^2 \phi)^{1/2}} \tag{19}$$

where H_1 is the unit vector in the direction of the earth's field at the point where I_ϕ is determined.

The magnetic potential at points on the surface of the earth along a noon meridian may then be determined by the aid of the relation

$$\Omega = -\iiint I_\phi \cdot \nabla(1/r) dV \tag{20}$$

where Ω is the magnetic potential. This expression has been formulated by a graphical integration at several points along a "noon meridian" at equinox.

The result of this integration taking account of the direction of the earth's field is shown in Fig. 1 which is expressed in terms of N_0. The horizontal component of the field due to the diamagnetic distribution was then determined by taking the space derivative of Ω along the earth's surface and its value in terms of N_0 is plotted in Fig. 2. Comparison with the observed values plotted in Fig. 3 shows that the form of the variations are

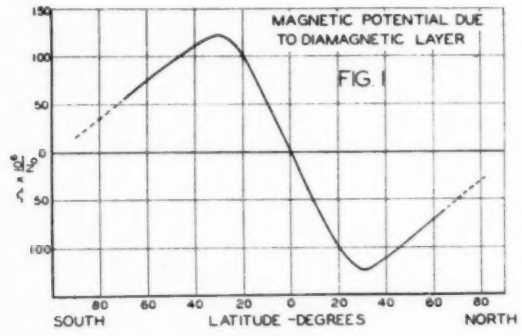

Fig. 1.

nearly identical. It will be observed that the horizontal component of this solar diurnal variation changes sign at about 30° latitude which is in good agreement with experimental observations. Agreement between theory and experiment is equally good in regard to the declination and vertical components of the field.

Measurements at the equator show that the earth's field at noon is on the average nearly 40 gammas (4×10^{-4} gauss) larger than at night. Assuming

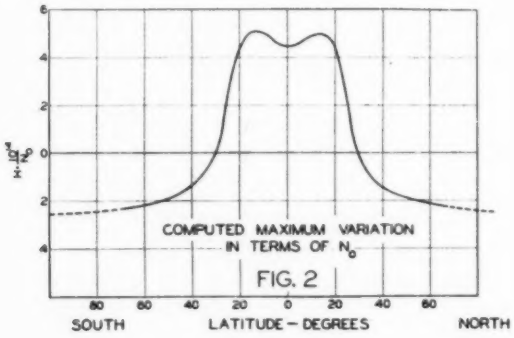

Fig. 2.

this value for the maximum value of the variation field in the foregoing theory the total number of ions of all kinds per cubic centimeter at the equator at noon is found to be $6\times10^{10}=N_0$. That is to say, the total number of ions per square centimeter at the equator at noon extending from the lowest layer where the free path becomes large on out to infinity must equal 18×10^{16}. It must be admitted that this is a large number since it requires

that an appreciable fraction of all the molecules present be ionized. Fortunately, no requirement is made in regard to the sign of the charge on the ions and the layer as a whole may be assumed to be nearly neutral. There appear to be no data contradicting the existence of such an intense ionization. Hulburt's[4] calculations of the upper atmosphere indicate that the recombination of ions in the region is slow and that there is sufficient ultra-violet energy

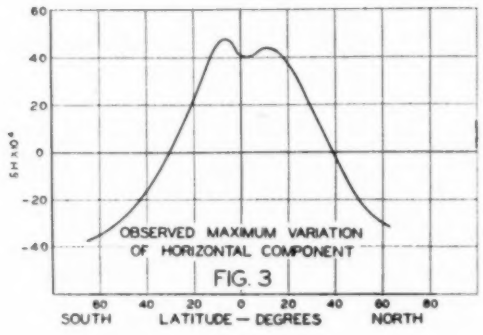

Fig. 3.

from the sun to replace those ions lost by recombination. Further, his calculations show that the number of ions necessary to explain the absorption of the longer radio waves is well within an order of magnitude of the number required on the present theory.

The situation in regard to the semidiurnal or lunar component of the magnetic variation is not quite so simple since it involves two independent phenomena; namely, the sun's ionizing effect and a tidal or other semidiurnal motion of the earth's atmosphere. Data available on the atmospheric tides indicate that tidal variations of semidiurnal character are extraordinarily regular. Such does not appear to be the case with the 24 hour or solar variation which is much more erratic. It is logical, therefore, to assume that the lunar variation is related to a true tidal effect or oscillation of the atmosphere while the solar variation is not. To bring the observed lunar diurnal magnetic variation into rough quantitative agreement with observation it is only necessary to assume that the mass motion of the neutral molecules of the diamagnetic layer due to their tidal motion communicate sufficient additional velocities to the ion bank to bring about variations having the same period as the tides. Assuming that on the average the distribution and intensity of ionization is the same as that determined for the solar component and that the ratio of the observed maximum variations is approximately 25, then by aid of Eq. (16) the maximum velocity of the tidal wind is found to be 10^4 cm/sec. This value may not be at all unreasonable at the high altitudes which are under consideration. Chapman[2] pointed out that there appeared to be no simple phase relation between the atmospheric tides and the semidiurnal magnetic variation. This is not at all surprising for it is reasonable to believe that there is a slight radial potential gradient existing

in the upper regions which will give rise to a preferential direction of motion of the ions toward the east or west, depending upon whether the field is the same or opposite to that at the earth's surface. Such a transport phenomenon is capable of explaining any reasonable phase shift of the magnetic effect and if we assume that the small residual charge in the upper atmosphere is such as to produce a field in a direction opposite to that at the surface of the earth the phenomena may be invoked to account for the occurrence of the maximum solar variation before high noon.

The type of variation of the earth's field occurring on so-called disturbed days may be qualitatively explained on the present theory in several possible ways. Observational data show that the maximum superimposed diamagnetic effect on disturbed days occurs at about sunset or a minimum effect at about sunrise, the variation being nearly sinusoidal in character with a 24 hour period. The simplest explanation fits with present notions, since it is only necessary to assume the presence of a strong ionizing agent, presumably a vertical ion stream which falls on the P.M. hemisphere of the earth. The presence of such a stream would increase the specific ionization as well as the temperature of the diamagnetic region and cause a large increase in the diamagnetic effect on the P.M. hemisphere. Conversely a sufficiently intense neutral molecular stream incident on the A.M. hemisphere might be expected to increase ion recombination greatly and produce a marked reduction of the diamagnetic field. This possibility is not viewed with favor.

It is difficult to understand just why an ion stream supposed to be nearly neutral as a whole should choose to fall on either the A.M. or P.M. hemisphere. It seems to be more logical, in view of the relative velocities of the ion stream and orbital velocity of the earth to assume the stream is incident for the most part on the hemisphere facing the sun. Such an assumption is capable of explaining the phenomena if we assume further that in addition to increasing the ionization and temperature of the region this ion stream produces either directly or by a redistribution of charge a radial electric field which is in the same direction as the electric field at the surface of the earth. Such a field will superimpose a translational motion in the direction of the earth's rotation on some of the ions formed and carry them well around to the P.M. hemisphere producing an intense ion bank in this region and explaining the observed effect. That such an electric field exists is pure assumption but is perhaps not improbable when we stop to reflect that the conductivity of the layer in the direction of the assumed field is very small.

The magnitude of this field at the equator may be determined from relation (8) by assuming the average transport velocity shall be slightly larger than the peripheral velocity of the earth. Taking, therefore $V_y = 5.0 \times 10^4$cm/sec. and $H = 0.3$ gauss, $E_z = 1.50 \times 10^{-4}$ volts/cm or a field roughly one ten-thousandth that at the surface of the earth which does not seem impossible.

A complete discussion of this theory would necessarily require a consideration of the effect of induced currents in the earth, and a more precise formulation of the ionic density distribution. To completely determine the

latter it will be found necessary to know more about the temperatures, electric fields and velocity of ions at high altitudes and more information must be available on the manner by which ionization in these regions increases with the length of exposure to ionizing radiations. Moreover, the direction of diffusion of the ions and the effect of the earth's magnetic gradient on the diamagnetic elements of the upper layers must be considered in a final and decisive analysis.

In view of our comparative ignorance of the physical facts it does not appear worth while to attempt a more detailed analysis of the problem at the present time.

HEAT AND LIGHT DIVISION,
NAVAL RESEARCH LABORATORY,
April 21, 1928.

THE ENERGY DISTRIBUTION OF COMPLEX MOLECULES

By Oscar Knefler Rice[1]

Abstract

It is shown that, for any distribution law in which Boltzmann's law holds for the various quantum states, $d \log W/dT = (\bar{\epsilon}_W - \bar{\epsilon})/kT^2$, where W is the fraction of the molecules in certain specified quantum states, $\bar{\epsilon}_W$ the average energy of the molecules in these states, $\bar{\epsilon}$ the average energy of all the molecules, T the absolute temperature, and k the gas constant. The distribution law will appear to be continuous if not viewed too closely, even though motions of the molecules are quantized. In what follows we consider the continuous outline and neglect the fine structure. If $W_\epsilon d\epsilon$ is the fraction of molecules whose energy lies between ϵ and $\epsilon + d\epsilon$, we have the general rule $\partial^2 \log W_\epsilon/\partial T \partial \epsilon = 1/kT^2$. Proceeding along these lines we can find in a new and simple way the distribution law over a range of energies if the average energy of the molecules (or the energy at which W_ϵ is a maximum) is given over a range of temperatures. At a given temperature we can compare the actual distribution law with a classical one which makes W_ϵ have a maximum at the same energy, and we find a limit beyond which the actual distribution law cannot depart from this particular classical law, provided the molecule is made up of a group of rotators and harmonic oscillators, and is sufficiently complex. An example is considered, which is of interest in the theory of the decomposition of azomethane.

IT IS frequently desirable, especially in connection with the theory of gas reactions,[2] to be able to make an estimate of the relative numbers of molecules of a complex gas which have various energies. This can be done if we make certain assumptions regarding the nature of the molecules. For example, we may suppose that they are composed of a certain number of classical rotators and oscillators. Or, again, we may suppose that the oscillators are quantized, but if we do this we must make definite assumptions regarding the frequencies involved.[3] In the case of actual molecules there must be many frequencies involved, and generally they are not known with any degree of certainty. Furthermore the greater the number of frequencies involved in our problem the more complicated it becomes. This suggests that we should try to throw the distribution law into a form which is independent of the particular frequencies involved, and investigate its general properties. The treatment which is given below is in fact quite independent of the structure of the molecule, though some propositions are considered which hold only of molecules whose energy can be expressed as a sum of squares of coordinates and momenta and which are sufficiently complex.

General Properties of the Distribution Law

We suppose that the molecule can exist in certain definite quantum states, and assume that the distribution between the various levels follows Boltz-

[1] National Research Fellow.

[2] See Rice, Proc. Nat. Acad. Sci. **14**, 113 (1928).

[3] See Kassel, Proc. Nat. Acad. Sci. **14**, 23 (1928); J. Phys. Chem. (in press).

mann's law. This may not be true at the very lowest temperatures, if we assume that something analogous to Pauli's exclusion principle holds for gas molecules, as has been shown by Fermi,[4] but will be very accurately true at all ordinary temperatures. We do not need to worry about any similar effect within the molecule, since we are interested in the distribution of all the energy among various molecules, not in the distribution of energy among the different parts of the same molecule, which, in any case, are presumably not affected by such considerations.

We let W be the fraction of the molecules which lie in certain specified quantum states, for example, those states which lie in a certain energy range. We let $\bar{\epsilon}_W$ be the average energy of the molecules in the states W, and $\bar{\epsilon}$ the average energy of all the molecules, k the gas constant and T the absolute temperature. We then have the following general theorem, which is an expression of the fact that the *a priori* probabilities are independent of the temperature:

$$d \log W/dT = (\bar{\epsilon}_W - \bar{\epsilon})/kT^2 \tag{1}$$

The proof of this is as follows[5]:

$$W = \sum_{i(W)} p_i e^{-\epsilon_i/kT} / \sum_i p_i e^{-\epsilon_i/kT}$$

where p_i is the *a priori* probability and ϵ_i the energy of the ith state, and where the summation in the numerator is to be taken over the states W and that in the denominator over all the states. Taking the logarithm of both sides and differentiating we get

$$\frac{d \log W}{dT} = \frac{\sum_{i(W)} p_i \epsilon_i e^{-\epsilon_i/kT}/kT^2}{\sum_{i(W)} p_i e^{-\epsilon_i/kT}} - \frac{\sum_i p_i \epsilon_i e^{-\epsilon_i/kT}/kT^2}{\sum_i p_i e^{-\epsilon_i/kT}}$$

But the fractions on the right hand side are simply $\bar{\epsilon}_W$ and $\bar{\epsilon}$ by definition of average.

Having proved this very general proposition let us now consider in some detail the general characteristics of the distribution law of a molecule of complex structure. If not viewed too closely it will appear to be continuous, on account of the various modes of quantization of the various parts of the molecule. Looked at more closely it will be seen to be in reality discontinuous. We shall, however, not concern ourselves with the fine structure, but only with the continuous outline, which is what we shall mean when we speak of the distribution law. We shall examine it with the aid of the theorem just proved.

If $W_\epsilon d\epsilon$ is the fraction of molecules having their energy in a certain small range ϵ to $\epsilon + d\epsilon$ the average energy in this range is practically ϵ, so

$$d \log (W_\epsilon d\epsilon)/dT = (\epsilon - \bar{\epsilon})/kT^2$$

[4] Fermi, Zeits. f. Physik **36**, 902 (1926).

[5] A similar proposition has been considered by Tolman, "Statistical Mechanics," p. 260 (Chemical Catalog Co., 1927).

Similarly for a range ϵ' to $\epsilon'+d\epsilon$

$$d \log (W_{\epsilon'} d\epsilon)/dT = (\epsilon' - \bar{\epsilon})/kT^2$$

Since $d\epsilon$ is independent of T it could be omitted from these equations. Subtracting one of these equations from the other

$$\frac{d \log W_{\epsilon'}}{dT} - \frac{d \log W_{\epsilon}}{dT} = \frac{d \log (W_{\epsilon'}/W_{\epsilon})}{dT} = \frac{\epsilon' - \epsilon}{kT^2} \tag{2}$$

This resembles the equation for the effect of temperature on an equilibrium constant.

If we divide Eq. (2) through by $\epsilon' - \epsilon$, and allow $\epsilon' - \epsilon$ to approach zero, Eq. (2) takes the form

$$\left[\frac{\partial}{\partial \epsilon}\left(\frac{\partial \log W_{\epsilon}}{\partial T}\right)_{\epsilon}\right]_T = \frac{\partial^2 \log W_{\epsilon}}{\partial T \partial \epsilon} = \frac{1}{kT^2} \tag{3}$$

This is true of any distribution law.

Finding the Distribution Law Over a Range of Energies from the Average Energy Over a Range of Temperatures

We shall use the above notions in the solution of a problem which is the converse of the one usually attempted, namely, we shall show how to find the distribution law for a range of energies if we are given the average energy of the molecules for a range of temperatures. This is a useful result, since we are often able to make some estimate as to the average energy.

Actually, however, we shall take as given, not the average energy, but the energy at which W_{ϵ} has a maximum, over a range of temperatures. These two quantities will not differ greatly in a complex molecule, and once a distribution law is constructed a relation between them can be found, and a second and further approximations made if necessary.

Now for a sufficiently small range of energies we may always set

$$W_{\epsilon} = B\epsilon^{(m-2)/2} e^{-\epsilon/kT}/(kT)^{m/2} \tag{4}$$

where m and B are independent of ϵ. By Eq. (2) or Eq. (3) m will be independent of T, but B may be a function of T since it does not affect the relative numbers of molecules which have different energies in the small range considered, but only the whole number which lies in the range. If the classical laws held, and if the energy of the molecule were expressible as a sum of squares, n in number, Eq. (4) with m set equal to n and B to $1/\Gamma(n/2)$ would hold over the whole range of energies, but with fixed values of B and m it can in general hold only over a small range in an actual case. For some other small range of energies different values of B and m must be used. Thus these quantities can in a sense be considered to be functions of ϵ, though in using

the distribution law (4) in the small range of energies in which it is approximately correct we regard them as constants. For our purposes it is going to be unnecessary to find the value of B; m can be approximately evaluated as follows. We take logarithms of both sides of Eq. (4) and differentiate, obtaining

$$\frac{\partial \log W_\epsilon}{\partial \epsilon} = \frac{m-2}{2\epsilon} - \frac{1}{kT} \tag{5}$$

Now we shall in general let T_ϵ be the temperature at which W_ϵ has a maximum at the energy ϵ. Then if ϵ is an energy lying in the range in which Eq. (4) is to be approximately true we get from Eq. (5), by setting it to zero for the proper energy and temperature,

$$(m-2)/2 = \epsilon/kT_\epsilon \tag{6}$$

T_ϵ is, by hypothesis, known as a function of ϵ. Eq. (6) may therefore be said to define m as a function of ϵ, since this will give the best value of m to use in the neighborhood of any given value of ϵ.

We may remark, in passing, since it is a conception that we are going to wish to use frequently, that m may also be considered to be, in a certain sense, a function of T. For we associate with every value of ϵ a temperature T_ϵ such that at T_ϵ the maximum of W_ϵ comes at ϵ, and there will be a one-to-one correspondence between values of ϵ and T_ϵ. If, however, we wish to think of T as the independent variable it will be convenient to write ϵ_T and T rather than ϵ and T_ϵ. Thus we would write Eq. (6) in the form

$$(m-2)/2 = \epsilon_T/kT \tag{7}$$

In general in an equation which contains m or ϵ_T (or both) and T we consider m and ϵ_T as functions of T, while if it contains m or T_ϵ (or both) and ϵ, we consider them as functions of ϵ; if no subscript is written T and ϵ are to be taken as independent variables.

If now we wish to find the relative number of molecules which have two different energies, ϵ_1 and ϵ_2, so far removed from each other that Eq. (4) cannot hold over that range, we may do it by integration of Eq. (5) replacing m by the function of ϵ we have found by use of Eq. (6). It is to be noted that in Eq. (5) T and ϵ appear as independent variables. In the integration T is held constant at some definite value, say T_0. The result is

$$\log (W_{\epsilon_2}/W_{\epsilon_1}) = \int_{\epsilon_1}^{\epsilon_2} \frac{m-2}{2\epsilon} d\epsilon - \frac{\epsilon_2-\epsilon_1}{kT_0} = \frac{\bar{m}-2}{2} \log (\epsilon_2/\epsilon_1) - \frac{\epsilon_2-\epsilon_1}{kT_0} \tag{8}$$

where $\bar{m}$ is a sort of average value of m. It is to be noted that we cannot replace m by the proper function of ϵ directly in Eq. (4) since we have evaluated m only after differentiating.

The problem which we set ourselves in this section is solved by means of this equation, or at least it can be solved by successive approximations, as suggested at the beginning of this section.[6]

Molecules Whose Energy Function is a Sum of Squares

The preceding considerations have been independent of any considerations regarding the structure of the molecule. It is often true, however, that we may consider, for a first approximation, that the molecules consist of groups of rotators and harmonic oscillators. Then the energy of a molecule is expressible as a sum of squares (n in number) of coordinates and momenta with constant coefficients, whether the motions of the molecule are quantized or not. In an actual case the oscillators will be quantized, while the rotators may be considered to act classically at all ordinary temperatures. The translational energy may also be assumed to be completely excited. If the molecules are sufficiently complex the individual molecules will all have energies fairly well bunched around the average energy, and the energy which makes W_ϵ a maximum will be fairly close to the average energy. The average energy will always be less than the classical energy, and will approach its classical value $nkT/2$ at high temperatures. In such a molecule it seems safe to assume that the energy, ϵ_T, which makes W_ϵ a maximum at a given temperature T is also less than the corresponding classical value, $(n-2)kT/2$, and approaches it as the temperature increases. If this is true $m<n$ and m gradually approaches n as T increases. Also, in the case we are considering $d\bar{\epsilon}/dT$ gradually approaches its classical value, and we shall assume that $d\epsilon_T/dT$ approaches its classical value $(n-2)k/2$. We may draw certain conclusions concerning the distribution law for a molecule such as is described above.

We shall be interested in comparing W_ϵ for any given energy at a fixed temperature T_0 with its value $W_{\epsilon_{T_0}}$ at the energy, ϵ_{T_0}, at which it has its maximum. We shall assume that we know the value of ϵ for which W_ϵ is a maximum at this particular temperature only, and shall then find two distribution laws, such that, if we plot $W_\epsilon/W_{\epsilon_{T_0}}$ against ϵ, the actual value of $W_\epsilon/W_{\epsilon_{T_0}}$ will lie between those given by the two laws. (Absolute values can always be found by means of the relation $\int_0^\infty W_\epsilon d\epsilon = 1$.)

One of these limiting curves will be the corresponding classical curve for the given temperature, which we shall define as the classical curve, in which W_ϵ has its maximum at the same value of ϵ as the actual curve. It is

[6] Another method of solving this problem has been worked out by Darwin and Fowler, Phil. Mag. **44**, 840 (1922). Their solution of the problem gives the distribution law with all its discontinuities, but the average energy must be known as a function of temperature over the whole range of temperatures. Its chief disadvantage, however, is that it requires a large number of mechanical integrations in the complex plane, and these would be practically impossible to carry out. It seems that in some cases it will be necessary to replace the "Zustandsumme" or partition function by a related function to insure the convergence of the integral in their definition of $J(q)$.

See also Fowler, Proc. Roy. Soc., **99A**, 462 (1921) and Ehrenfest, Ann. d. Physik. **36**, 111 (1911).

found from Eq. (4) by setting m constant and equal to the value given by Eq. (7) for the temperature T_0 and energy ϵ_{T_0}. Since the real m is an increasing function of ϵ, it will be found, if we put $\epsilon_1=\epsilon_{T_0}$ in Eq. (8) that the actual distribution $(W_\epsilon/W_{\epsilon_{T_0}})$ spreads more on either side of the maximum than the corresponding classical distribution; or, in other words, its maximum is not as sharp as the classical one.

We now find another limiting curve, such that the actual curve must lie between it and the corresponding classical curve, in the following manner. From Eq. (7) we have (regarding m now as a function of T, as explained in the previous section)

$$\frac{1}{2}\frac{dm}{dT}=\frac{d\epsilon_T/dT}{kT}-\frac{\epsilon_T}{kT^2}=\frac{d\epsilon_T/dT}{kT}-\frac{m-2}{2T} \tag{9}$$

Now the greater dm/dT the greater will be the deviation from the result of setting m constant in Eq. (8). In the case we are considering $d\epsilon_T/dT$ will gradually approach its classical value $k(n-2)/2$, and is actually less than this value. If we substitute this classical value in Eq. (9) we get

$$dm/dT=(n-m)/T \tag{10}$$

which gives a greater value than dm/dT can actually have. n being constant, this is easily integrated to give

$$(m-n)/2=c/T \tag{11}$$

c is a constant of integration which we determine from the value of m, at the temperature T_0, given by Eq. (7). The value of m then obtained from Eq. (11) must be greater or less than the true value of m depending upon whether T is greater or less than T_0. If we wish to consider ϵ as independent variable rather than T, we can indicate this by writing Eq. (11)

$$(m-n)/2=c/T_\epsilon \tag{12}$$

Consider now the equation[7] $d\epsilon_T/dT=k(n-2)/2$, which we used in getting Eq. (12). If we want to make ϵ the independent variable in this equation we write it

$$d\epsilon/dT_\epsilon=k(n-2)/2 \tag{13}$$

Inverting and integrating from ϵ_{T_ϵ} to ϵ we get

$$T_\epsilon=T_0+2(\epsilon-\epsilon_{T_0})/k(n-2) \tag{14}$$

This is of the same form as a classical equation in which the number of energy terms is equal to n, but is not such an equation at all, since the quantities ϵ_0 and T_0 which we started with were not classically related. It represents the variation of T_ϵ with ϵ which we used to obtain Eq. (12), and it may con-

[7] Not really a true equation but a limiting form.

sequently be substituted in Eq. (12) without inconsistency. c has the value determined as above. This enables us to get a value of m as a function of ϵ, the value of m thus obtained being greater or less than the true value of m if ϵ is greater or less, respectively, than ϵ_{T_0}. If the result is put into Eq. (8) and the integration with respect to ϵ performed, letting $\epsilon_1=\epsilon_{T_0}$ and $T_{\epsilon_1}=T_{\epsilon_{T_0}}=T_0$ and writing ϵ instead of ϵ_2 in the final result we get

$$\log (W_\epsilon/W_{\epsilon T_0})=\frac{n-2}{2}\log\left(1+\frac{2(\epsilon-\epsilon_{T_0})}{kT_0(n-2)}\right)-\frac{\epsilon-\epsilon_{T_0}}{kT_0} \qquad (15)$$

This is the limiting curve we have been striving for, the value of $W_\epsilon/W_{\epsilon T_0}$ calculated from it being always greater than the actual value of this quantity. Indeed, we can probably count on the value of $W_\epsilon/W_{\epsilon T_0}$ thus calculated considerably exceeding the actual value of the quantity.

Application to a Special Problem

We shall illustrate these considerations by an application to a problem which concerned us in the quantum theory treatment of the decomposition of azomethane.[8] We wished to find whether there was a large chance that, if a molecule of 54,000 calories per mole energy should collide with an average molecule which we estimated to have 6,000 calories per mole at the temperature of interest, either molecule should emerge from collision with more than 50,000 calories per mole. (These are internal energies, as in these considerations we were not interested in translational energies.) This is the same as finding the chance that one of the molecules should have more than 50,000 or less than 10,000 calories per mole. The chance would be 1/3 if a molecule were as likely to have one energy as another after collision. In order to find the chance that the molecules should have widely different rather than nearly equal energies we attempted to compare the probability that both molecules should have 30,000 calories per mole with the chance that one of them should have 50,000 and the other 10,000.

We assume that statistical equilibrium is established between the various degrees of freedom at a collision. Then the ratio of the probability that one will have 10,000 and the other 50,000 calories per mole to the probability that both will have 30,000 calories per mole is given by $W_{10}W_{50}/W_{30}^2$ where W_{10} is the probability (per unit energy range) calculated from the distribution law that a molecule should have 10,000 calories per mole, etc.[9]

This ratio is independent of temperature as is readily seen from Eq. (8), since $\bar{m}$ is independent of T_0, or from the fact that the result of a collision of definite energy cannot depend upon the temperature. We may accordingly assume the temperature to be such that W_{30} is the maximum value of W_ϵ at that temperature. This temperature will be approximately that at which 30,000 is the average energy, and we have previously estimated it to be about 1250°C, abs.[8] Then by using Eq. (15) we find (n is 51 in the case

[8] Rice, Proc. Nat. Acad. Sci. **14**, 122 (1928).

[9] See Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1622, 1625 (1927).

of azomethane, excluding the translational terms) $W_{10}W_{50}/W_{30}^2 = 0.064$· 1250° may be a little low, since the average energy is probably higher than the energy of the maximum, but had we used 1500 for T_0, a value which seems certainly too high, we should have obtained 0.15. Since using Eq. (15) gives us a result which is too large, these figures give us some confidence that for the purposes of our previous considerations we may neglect the chance that a molecule should emerge from collision with more than 50,000 calories per mole.

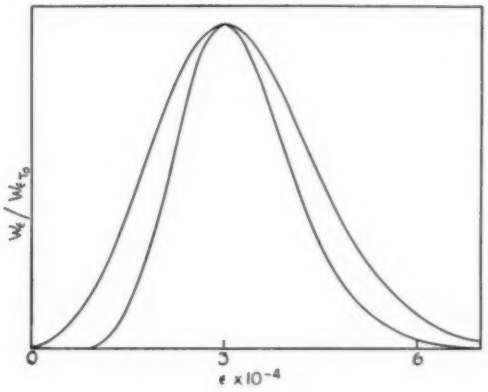

FIG. 1

In order to illustrate the sort of range in which the distribution law may lie we have plotted in Fig. 1 the two extreme distribution curves in the case just considered. Assuming that at 1250°C, abs., $\epsilon_T = 30{,}000$ calories per mole, we calculate from Eq. (7) that m is 26. Assuming that it is constant at this value we get the lower curve in Fig. 1. Using Eq. (15) we get the upper curve.

GATES CHEMICAL LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
January 19, 1928.

BOOK REVIEWS

The Chemical Effects of Alpha-Particles and Electrons. S. C. LIND. A. C. S. Monograph Series. 2nd Edition. 260 pages. The Chemical Catalog Company, Inc., New York, 1928. Price, $5.00.

In the preface to the second edition the author says: "The progress since 1921 in the study of radiochemical effects has necessitated a complete revision and the addition of seven new chapters. The changes consist mainly in the expansion of the principles announced in the first edition rather than in their radical alteration." The period since the first edition of Lind's monograph marks indeed considerable progress in the particular field of radiochemistry covered by his book, progress which is due in particular to the fundamental researches of the author and his collaborators. The material newly presented deals mainly with the more quantitative correlations between gaseous ionization and chemical effects of alpha-particles, the catalytic action of ions of foreign gases, reactions of hydrocarbons and the close similarity of the reaction mechanism of the hydrogen-chlorine combination by the action of light and by alpha-particles. The volume contains, furthermore, besides an introductory chapter on radioactivity, sections on gaseous ionization, effects produced in minerals, glasses, and other solid bodies, reactions in liquids and, particularly, in gaseous systems, effects of recoil atoms, chemical effects of electric discharges, atomic disruption and a short review of the photochemical Equivalence Law.

The book offers a comprehensive and critical survey of experimental data obtained in a field where the processes involved are complicated and numerous. For their interpretation, the author applies the results of more physical investigations on the effects of alpha-particles and fast electrons, production of gaseous ions and their properties, achieving in this way very considerable success.

This book can be recommended not only for study by those interested in the particular field, but also for a more general use as a reference work. The volume is even more valuable for this last purpose because it contains numerous references to original literature easily accessible with the aid of very complete author and subject indexes.

G. B. KISTIAKOWSKY

Matter, Electricity, Energy. WALTER GERLACH. Translated by J. Fuchs. Pp. 439, 119 figs. D. Van Nostrand Company, New York. Price, $6.00.

The subtitle of this book is "Principles of Modern Atomistics and Experimental Results of Atomic Investigation." The contents are well described by this. The material is largely experimental. No attempt is made to treat any particular subject exhaustively. A considerable number of topics is touched upon. Separate chapters are devoted to isotopes, atomic rays, dipoles, nuclear disintegration, electronic charge, the magneton, super-conductivity, crystal conduction, several chapters on emission and absorption phenomena including x-rays, resonance and dispersion, the far infra-red and the ultra-violet regions, the photoelectric effect, crystal structure, photochemistry, radiation measurements, astrophysics, and some others. The book was essentially completed in 1923 so that neither the newer spectroscopic developments nor the new mechanics have been included. Even the older spectroscopic material is barely touched upon. The book has been obviously not intended for physicists but rather for those who wish to know what modern physics is about.

G. BREIT

Abhandlungen zur Wellenmechanik. E. SCHROEDINGER. Pp. 197, 14 figs. Second enlarged edition. Johann Ambrosius Barth, Leipzig, 1928. Price, unbound R. M. 6.80; bound R. M. 8.30.

In addition to the six articles reprinted in the first edition, three newer ones are included. These are on: (1) The Compton effect; (2) Energy-momentum relations for waves representing

matter; (3) Exchange of energy for undulatory mechanics. The Compton-effect treatment gives a diagrammatic representation of the relations between the ψ waves and the reflected electromagnetic radiation.

The energy-momentum relations contain, in addition to the derivation of Gordon's expression for the current-density fourvector, a formulation of the variation principle which yields Maxwell's equations and the conservation theorem for the momentum-energy tensor of the wave fields of matter and electromagnetic radiation taken together. The significance of this article has remained so far purely formal. The reasons for this are pointed out in the article.

The last paper of the series gives a simple treatment of the problem of coupled systems. The author formulates the view that it may be narrow-minded to think of atoms as being definitely in one state or in another. Experiments on electron impact are to be interpreted in terms of resonance rather than change of state. An outline of a treatment of statistics in the new mechanics is given.

G. BREIT

Handbuch der Elektrizität und des Magnetismus. L. GRAETZ. Band V, Lieferung 2. Pp. 357, 365 figs. Johann Ambrosius Barth, Leipzig (1928). Price, unbound, R. M. 29.00.

The book is written in the form of a more or less advanced text book rather than from the information point of view desired in a handbook as the title specifies. The factors treated upon the d. c. machine are of suffiicient depth to give a clear understanding of all factors involved. The design of this machine has received careful consideration. Commutation with interpoles and the D^2L relations have not been emphasized. The operation under the conventional steady state has received consideration whereas the transients in d. c. machines have been omitted. Special machines as the Rosenberg and Kraemer machines have received a brief mention whereas the common 3-brush automobile generator received no attention. The diagrams and illustrations upon the d. c. machine and detail are very good. The various types of winding receive special consideration.

The alternating generator also receives very careful consideration with all factors influencing the fundamental frequency of current and voltage. The harmonics and factors influencing their design receives little consideration. The parallel operating characteristics and stability of a. c. generators has also received a very protracted treatment. The constructional details of this machine are very good. A design of detail is also included for one machine.

The transformers of all types receive twenty-four pages primarily of descriptive material and of little value to the transformer engineer. The induction motor also receives little more than scant mention. Some little space is given to self-excited induction motors and circuits involved but design factors and operating characteristics are not considered. The convertor treatment by Max Zorn is largely descriptive, touching upon split pole and other factors at present of little service in American practice. The Mercury Convertor by Jungmichl contains a very careful description and will be of interest to all mercury convertor operators. The chief underlying factors are carefully illustrated. The work on the whole is very creditable even though it lacks systematized treatment by the various contributors. Regulation and control equipment used in conjunction with this machinery has also been omitted. From the standpoint of a handbook, it is very incomplete.

F. W. LEE

Music: A Science and an Art. JOHN REDFIELD, formerly lecturer in Physics of Music Columbia University. Pp. 332, 22 figs. Alfred A. Knopf, New York (1928). Price, $5.00.

This work deals with a great variety of musical problems, not only those purely or approximately scientific, such as the nature of sound impulses, the harmonic series, the derivation of the scale, and the theory of harmony, but those approximately or purely artistic, such as the improvement of musical instruments, the development of the voice, and the nature of musical beauty. The point of view toward all these problems is that of the laboratory worker, and the tests applied are of a scientific character; but the conclusions reached are sometimes so at variance with current belief and practice as to excite considerable question of the validity of the author's reasoning.

The purely physical problems are admirably dealt with; the discussion of the tempered scale, and the formulation of a new and better substitute for that scale being easily intelligible to the reader not technically trained.

But as soon as the aesthetic element enters the question, Mr. Redfield's reasoning begins to be flawed. Although he insists that music is not something on a sheet of paper, but is something to be heard, he seems to restrict the scope of that hearing process to acoustics, and to ignore the values of imagination. To the musical mind harmony is not merely an acoustical relation of consonance and dissonance, but a musical *idea;* and while perfection of tuning is greatly desirable, it is a condition of the utterance of the idea, not the idea itself. Thus the assertion that "the sense of harmony is as extinct as the dodo" is incapable of proof by the demonstration of faults in our present tuning.

The same attitude blinds the author to the uselessness of most of his projects for improving the practice of musical art. For instance, as an aid to orchestration, he would provide an enormous library of phonograph records, illustrating every possible instrumental combination. He forgets that orchestration is only remotely an acoustical problem; that the composer's *idea* dictates his choice of instruments; and that this bewildering list of records would be a mere color-card, looked at in a paint-shop, away from the room to be decorated. Orchestration is not a job for the handy man around the house.

Faith in the laboratory method could scarcely further go than in the following gem: "Put a violin in the hands of an able civil engineer—one capable of designing a suspension bridge—furnish him with a moderate amount of fundamental information about sound, tell him to improve the instrument, and in a year or so he will turn out such a violin as Stradivarius dreamed of all his life but never succeeded in building. If this be blasphemy, make the most of it." This isn't blasphemy. It is only Menckenese.

As an indication of the shallowness of current thought about music this book is depressing. For it is the sober truth that there is more thought about music in it than in any work issued for many years. Its scientific contribution is positive. Its artistic contribution is largely negative; but, in the present state of musical thought it has the value of raising a great many questions about which it compels the reader to think.

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